1988

Transition metal carbene complexes and platinum-catalyzed substitution of metal carbonyls

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Order Number 8825463

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Transition metal carbene complexes and platinum-catalyzed substitution of metal carbonyls

by

Shian-Jy Wang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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For the Major Department

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For the Graduate College

Iowa State University
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1988

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DEDICATION

To my mother, father, and my husband, Weir-Mirn

PREFACE

The research presented in this thesis addresses two aspects of organometallic chemistry. The first topic is the reactivity studies of dioxycarbene ligand in $Fe(CO)_4(=\overline{COCH_2CH_2O})$ and aminooxycarbene complex, $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ in which CO is replaced by phosphine or hydrotris (pyrazolyl) borate ligands, the Br is replaced by CH_3, and the H on the carbene N is replaced by CH_3.

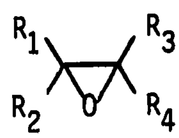
The second area of research is the substitution reactions of metal carbonyls. This type of reaction is commonly carried out under photochemical or thermal conditions. However, two Pt(0) compounds, $Pt(PPh_3)_4$ and $Pt(dibenzylideneacetone)_2$, catalyze phosphine substitutions of metal carbonyls and offers a convenient, high yield route to monosubstituted products.

This thesis consists of four sections, with the first comprising a literature review of transition metal promoted reactions of epoxides. The following sections represent the research as they are submitted for journal publication. Each section contains references, tables, figures, and equations pertinent only to the particular article.

SECTION I. A REVIEW OF TRANSITION METAL PROMOTED REACTIONS OF EPOXIDES

INTRODUCTION

Epoxides are cyclic three-membered ethers (oxiranes). They are



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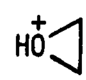
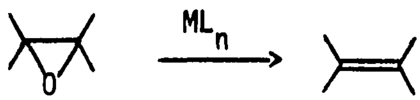
extremely valuable because of the many reactions they undergo. Ethylene oxide (1; $R_1 = R_2 = R_3 = R_4 = H$) was first prepared by Wurtz in 1859 [1], by the reaction of 2-chloroethanol with aqueous potassium hydroxide. Many other investigators tried to prepare ethylene oxide by direct oxidation and failed until Lefort [2] succeeded in the direct oxidation of ethylene to ethylene oxide over a silver catalyst.

The total annual United States sales value of ethylene oxide exceeds $\$10^9$ making it one of the most significant organic chemical products [3]. Ethylene oxide is a highly reactive molecule. The three-membered ring is opened in most of its reactions with compounds such as ammonia, organic acids, alcohols, and water; however, in reactions with strong anhydrous mineral acids [4], oxonium salts are formed, 

. Ethylene oxide polymerizes under thermal ionic and free-radical catalysis. There is a considerable amount of research on epoxy homopolymers and copolymers for industrial applications. In this section, reactions of epoxides will focus on deoxygenation, rearrangement and carbonylation which are promoted by transition metals.

DEOXYGENATION

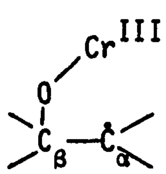
The deoxygenation of epoxides to olefins is an important reaction in organic synthesis (eq. 1). The epoxide is employed either as a protecting



(1)

group [5] or as a key intermediate in the stereochemical transformation of an olefin. The transition metal complexes which are capable of reducing epoxides to olefins can be grouped broadly into three categories: (1) Class I species, e.g., $Cr^{II}(H_2NCH_2CH_2NH_2)$ ($Cr^{II}en$), $TiCl_3$-$LiAlH_4$ ($TiCl_3$-LAH), WCl_6-LAH and β-diketonate complexes of V^{II} and Mo^{II}, promote nonstereospecific deoxygenation of oxiranes to olefins. (2) Class II species, e.g., WCl_6+n-BuLi and $M(C_5H_5)_2$ (M = Mo, W) give rise to olefins with a predominance of retention of stereochemistry from either cis- or trans-epoxides. (3) Class III species, e.g., $Co_2(CO)_8$, reduce epoxides with inversion of the epoxide stereochemistry.

The nonstereospecific reduction of epoxides to olefins can be explained by a mechanism which involves radicals as intermediates. Kochi et al. [6] studied the reduction of epoxides by Cr^{II}(en). They propose that this reduction proceeds via essentially two routes: Cr^{II}(en) attacks at oxygen or carbon to generate either **2** or **3**, respectively. The evidence



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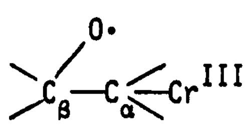

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which supports the favorable intermediate 2 comes from the 2,3-epoxymesityl oxide and styrene oxide showing a greater reactivity than cyclohexene oxide; because the C-centered radical 2 should be stabilized more by a CO or phenyl group on the C_α than 3. Further reaction with Cr^{II}(en) gives β-oxyalkyl chromium intermediate 4 (Figure 1.1) followed by reductive elimination to olefin and Cr^{III}. Other reducing metals or metal salts such as $TiCl_3$-$LiAlH_4$ [7] and WCl_6-$LiAlH_4$ [8] belong to this group. They probably follow a mechanism similar to that of the related chromous ion reduction.

Another mechanism is proposed for the reaction of epoxides and β-diketonate complexes of V(II) and Mo(II) [9]. The stereospecificity of deoxygenation depends on the size of substituents on the epoxide ring and on the β-diketonate ligands. The initial intermediate of reaction between the reduced metal species and the epoxide is an open-chained one (as suggested in Figure 1.2) which can be configurationally trapped by C-M bond formation giving a cyclized metallooxetane, hence to yield olefin. Competitive C-C bond rotation leads to nonspecific olefin formation. Increasing the alkyl group size on epoxides leads to an increase in stereospecificity (as demonstrated in Table 1.1). This is because the presence of bulky alkyl substituents on the C-C unit in the epoxide decrease the rate of rotation around the C-C bond. Also, reducing the congestion about the metal (larger ionic size of Mo^{II} in comparison with V^{II} and smaller substituents on the diketonate ligands) enhances the cyclization rate, thus increasing the stereospecificity of epoxide deoxygenation.

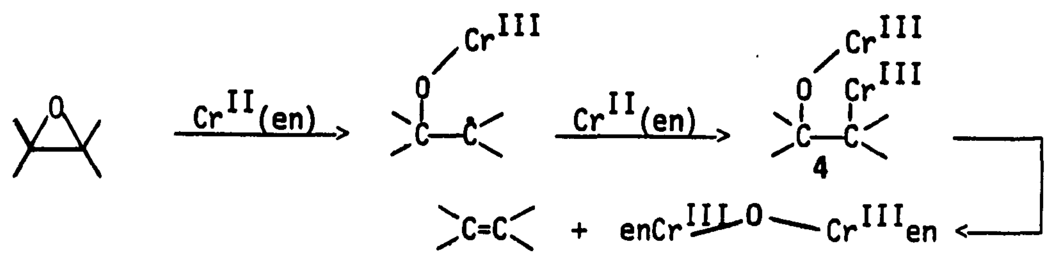


Figure 1.1. Proposed mechanism of nonstereospecific deoxygenation of epoxides to olefins by $Cr^{II}(en)$

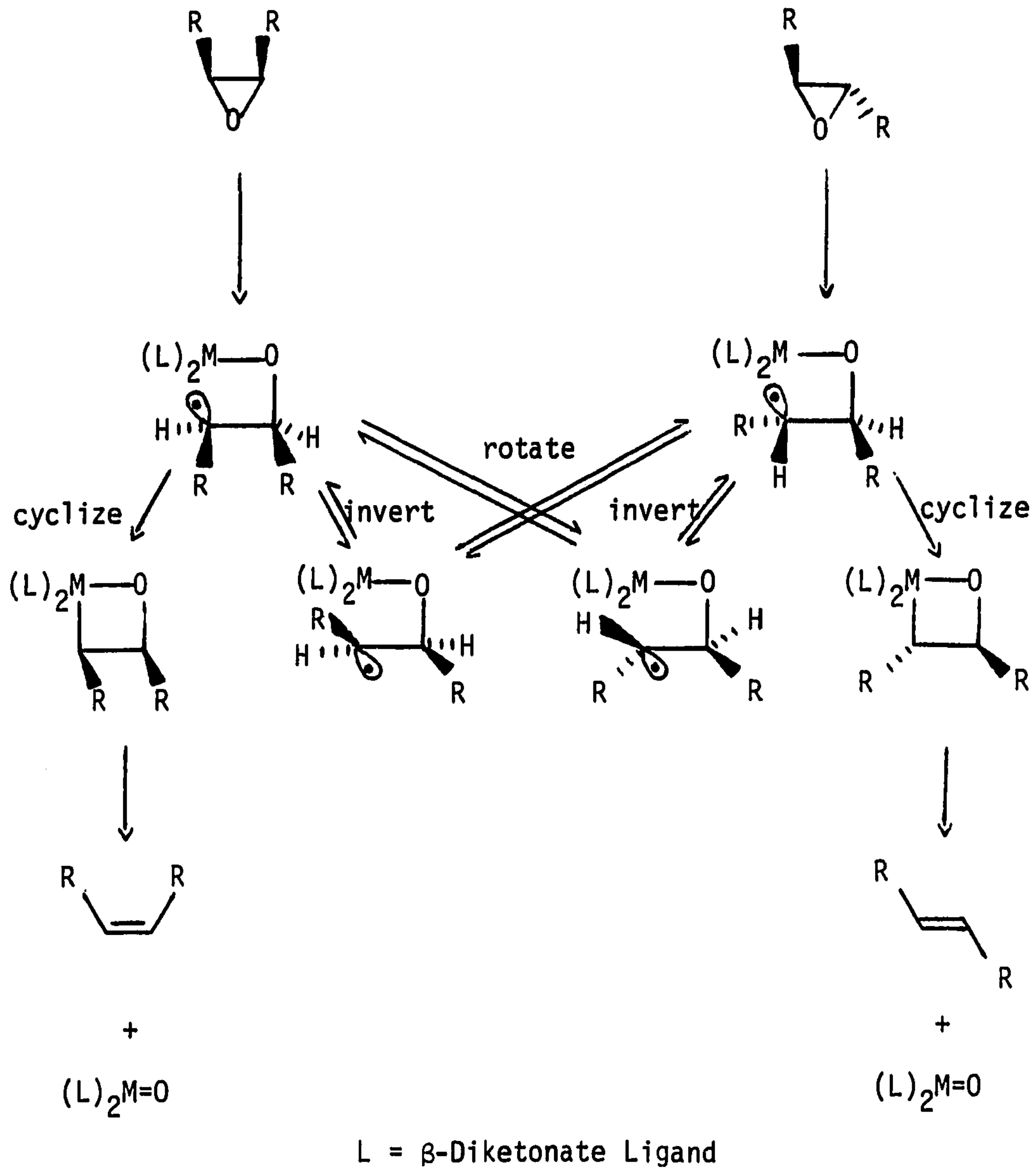
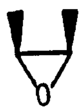
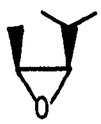
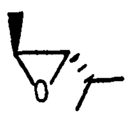
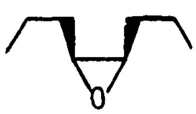
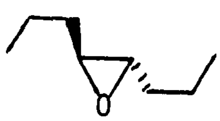


Figure 1.2. Two proposed pathways involving diradicals or metallooxetane of deoxygenation of epoxides

Table 1.1. Deoxygenation of epoxides to olefins

Epoxide	Reagent[a]	% Olefin Yield	Stereochemistry cis	Stereochemistry trans
	$V(acac)_2$	88	51	49
	$V(dpm)_2$	~100	42	58
	$V(tfa)_2$	41	44	56
	$Mo(acac)_2$	61	72	28
	$V(acac)_2$	45	41	59
	$V(dpm)_2$	~100	43	57
	$Mo(acac)_2$	66	25	75
	$V(acac)_2$	44	43	57
	$V(dpm)_2$	~100	43	57
	$Mo(acac)_2$	95	83	17
	$Mo(dpm)_2$	~100	77	23
	$V(acac)_2$	88	32	68
	$V(dpm)_2$	92	42	58
	$Mo(acac)_2$	93	15	85
	$Mo(dpm)_2$	98	22	78
	$V(acac)_2$	82	47	53
	$V(dpm)_2$	99	45	55
	$V(tfa)_2$	56	41	59
	$Mo(acac)_2$	99	84	16
	$Mo(dpm)_2$	96	75	25
	$V(acac)_2$	82	33	67
	$V(dpm)_2$	~100	44	56
	$Mo(acac)_2$	79	14	86
	$Mo(dpm)_2$	83	19	81

[a]Acac = 2,4-pentanedionate, $CH_3\overset{O}{\overset{\|}{C}}CH\overset{O}{\overset{\|}{C}}CH_3$; dpm = dipivaloylmethonate, $Me_3C\overset{O}{\overset{\|}{C}}CH\overset{O}{\overset{\|}{C}}CMe_3$; tfa = 1,1,1-trifluoroacetylacetonate, $CF_3\overset{O}{\overset{\|}{C}}CH\overset{O}{\overset{\|}{C}}CH_3$.

The reduction reaction of epoxides with Na(η^5-C_5H_5)Fe(CO)$_2$ [10] (NaFp) results in the alkoxides **5** (Figure 1.3). Upon reaction in situ

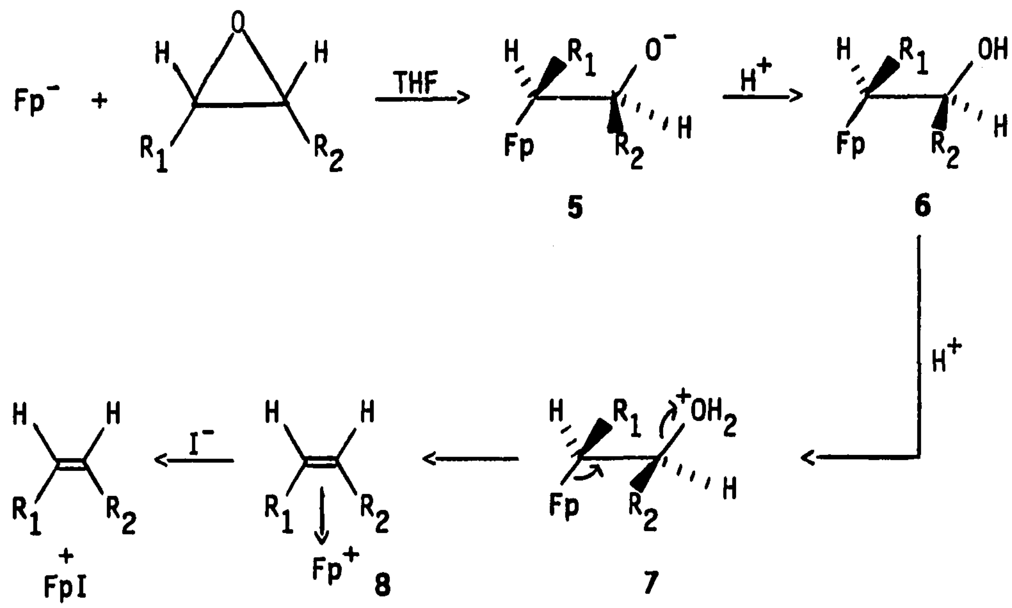
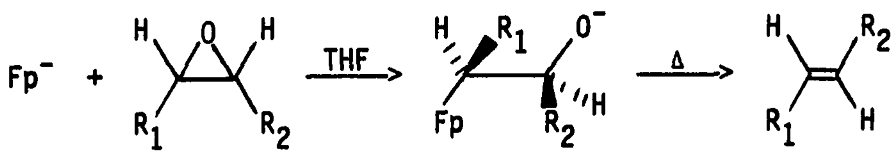


Figure 1.3. The sequence for retained stereochemistry deoxygenating epoxides to olefins by Na(η^5-C_5H_5)Fe(CO)$_2$

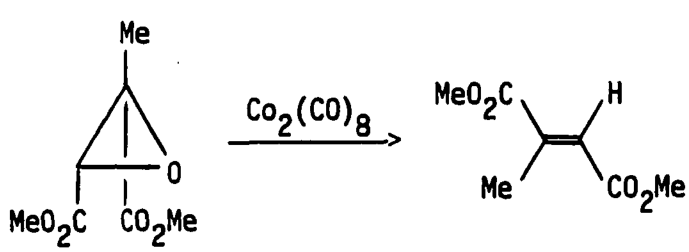
with two equivalents of hexafluorophosphoric acid, **5** is converted instantaneously and in high overall yield to the olefin π-complexes **8**. The olefin salts are transformed readily at room temperature by treatment with sodium iodide in acetone, liberating the olefins. The conversion of epoxide to olefin proceeds with retention of configuration as is indicated by the conversion of cis and trans-2-butene epoxides to the stereochemically unchanged olefins (> 98% retention). The stereochemical result may be understood by a mechanism involving an initial S_N2 opening of the epoxide ring by the complex anion followed by the protonation of the alkoxides **5** formed the oxonium ion **7**. The intermediate alcohol **6** is isolated as an air-sensitive solid by reacting a solution of **5** with water. Then, a trans-elimination of **7** concerted with the loss of water gives olefin π-complexes **8**. However, the intermediate alkoxides **5** are thermally decomposed [11] to generate the olefins are produced with inverted stereochemistry (eq. 2). The detailed mechanism is not yet clear; it may involve a cis-elimination, since epoxide opening by Fp^- has been shown to



5

(2)

occur with inversion [10]. Deoxygenation with $Co_2(CO)_8$ also causes inversion of the epoxide stereochemistry in the olefin product [12]. If cis-dimethyl epoxy methyl-succinate **9** is treated with a catalytic amount of $Co_2(CO)_8$ for 18 h, a 95% yield of trans-dimethyl-mesaconate **10** is obtained (eq. 3). However, the mechanism for this deoxygenation of epoxides with inversion of stereochemistry is not yet understood.



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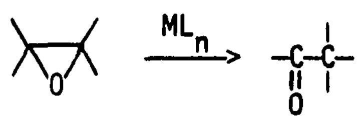
(3)

REARRANGEMENT

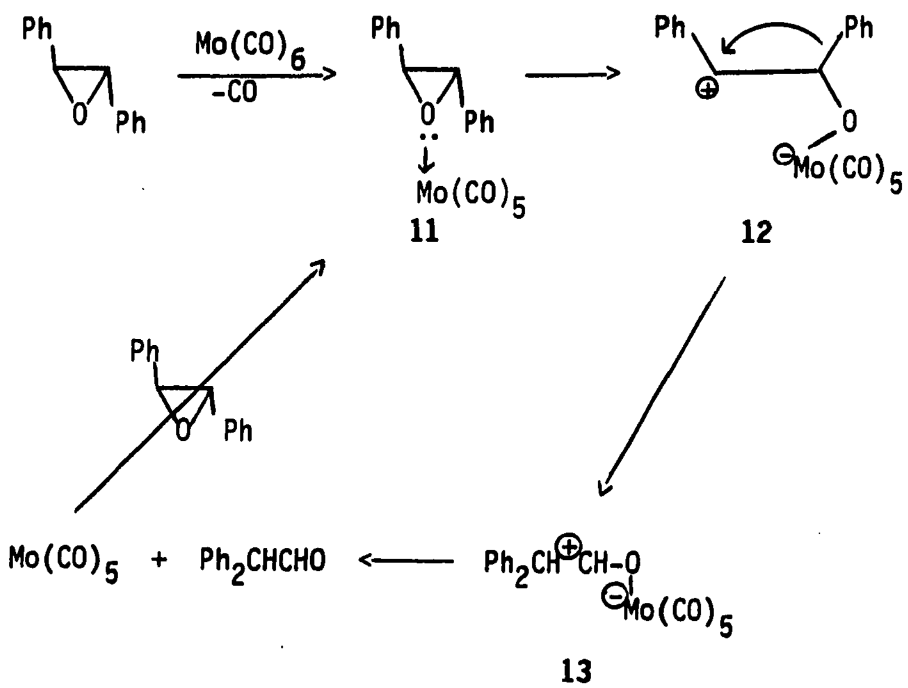
Epoxides may be rearranged to aldehydes or ketones by several transition metals and transition metal complexes (eq. 4). For example,



(4)

$Mo(CO)_6$ is known as a homogeneous catalyst for the rearrangement of epoxides to aldehydes [13]. A by-product of these reactions is a deoxygenated olefin with retained stereochemistry with respect to the epoxide.

The mechanism of the epoxide rearrangement is shown in Figure 1.4. Evidence for this mechanism comes from studies of epoxides which are not capable of forming stable carbonium ions (e.g., 2,3-epoxide-propyl-p-methoxyphenyl ether). They do not undergo rearrangement. The proposed mechanism is shown in Figure 1.4. Initial epoxide complexation of the $Mo(CO)_5$ moiety affords complex **11**; then, C-O bond cleavage gives the stable benzylic carbonium ion **12**. By phenyl migration, **12** rearranges to **13**. Decomplexation of **13** produces the aldehyde and $Mo(CO)_5$ which continues the catalytic cycle by further complexation with the epoxide. The deoxygenated by-products may be due to the interaction of the epoxide oxygen with a carbonyl carbon of the metal carbonyl to give **14** which then collapses to olefin, CO_2 and the $Mo(CO)_5$ moiety. A similar mechanism has been proposed for the deoxygenation of sulfines and other organic a)



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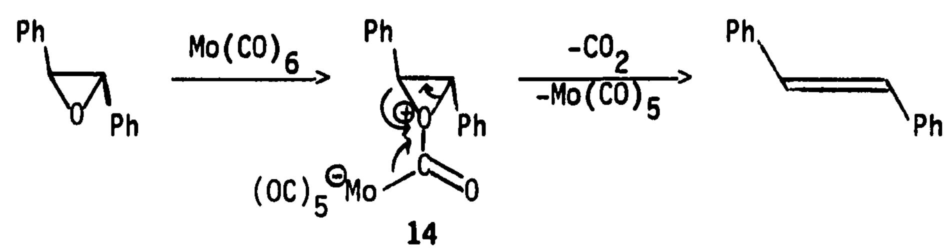
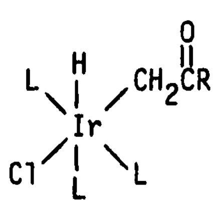


Figure 1.4. The proposed mechanism of rearrangement and deoxygenation of epoxides by $Mo(CO)_6$

compounds containing S-O or N-O bonds by $Mo(CO)_6$ [14]. $W(CO)_6$ was an ineffective catalyst for rearrangement reactions of epoxides (eq. 4) possibly because the dissociation of CO from $W(CO)_6$ is slower than that of $Mo(CO)_6$. Under UV irradiation, $Fe(CO)_5$ also induces the isomerization and deoxygenation of epoxides [15]; however, a thermally induced reaction of $Fe(CO)_5$ with epoxides in tetramethyleneurea at 145°C causes only deoxygenation [16]. When $Fe(CO)_5$ is used as a catalyst, trans-stilbene oxide is converted to cis-stilbene and benzylphenylketone under photolytic conditions. In contrast, the products of the $Mo(CO)_6$-catalyzed reaction of trans stilbene oxide are diphenylacetaldehyde and trans-stilbene (Fig. 1.4); the proposed mechanism involves the free carbocation intermediate, **12**. Therefore, the coordinated intermediate **15** appears to be preferred in the $Fe(CO)_5$-catalyzed reactions, as shown in Figure 1.5.

The oxidative-addition reaction of epoxides with the Ir(I) trimethylphosphine complex, $Ir(C_8H_{14})(PMe_3)_3Cl$, (**18** C_8H_{14} = cyclooctene); sheds light on the mechanism of the transition metal catalyzed transformation of epoxides to aldehyde [17]. The reaction of **18** with ethylene oxide, propylene oxide or styrene oxide affords the Ir(III)-cis-hydrido-alkyl complexes **19**, **20**, and **21**, respectively. On the other hand, **18** reacts



L = PMe_3

19 R = H
20 R = CH_3
21 R = Ph

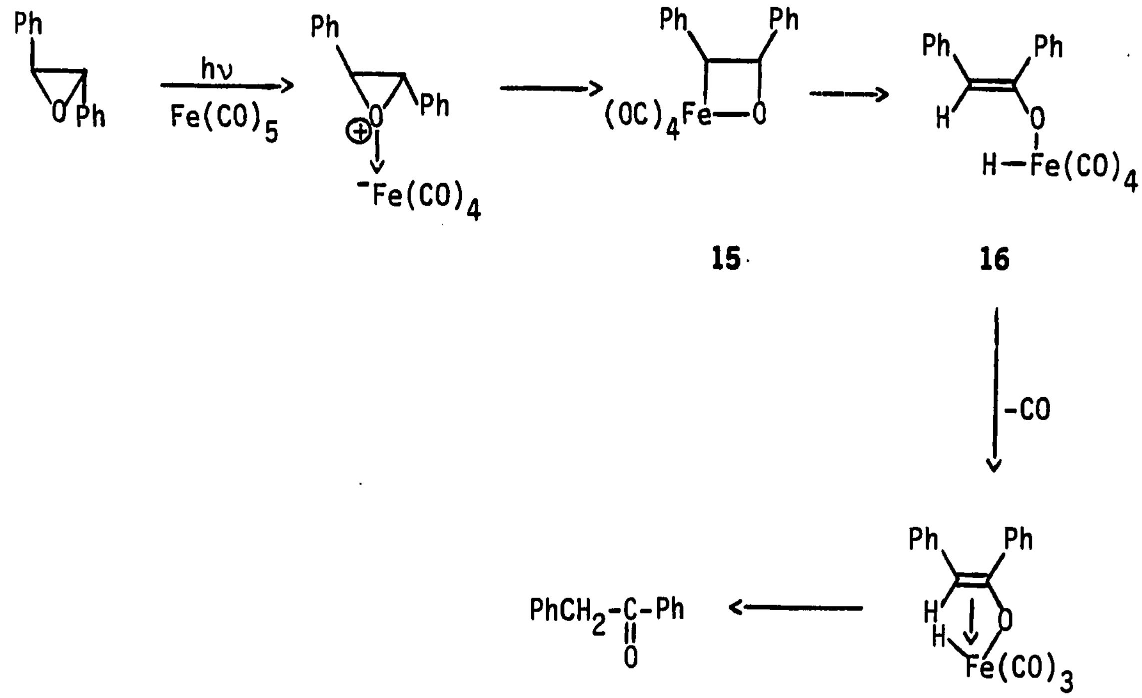
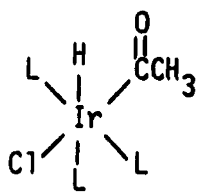


Figure 1.5. The proposed mechanism of epoxides rearrangement by $Fe(CO)_5$ under UV irradiation

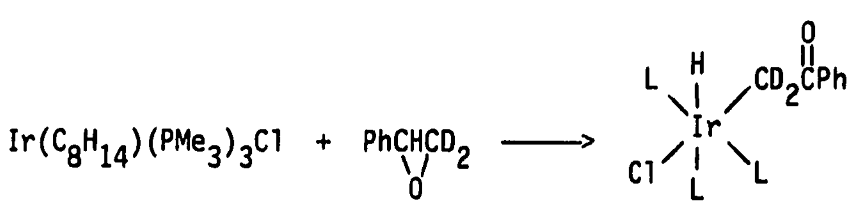
rapidly with acetaldehyde to yield the cis-acetylhydridoiridium (III) complex, **22**. This excludes the possibility that the epoxides rearrange to aldehydes then react with **18**. The proposed mechanism of this reaction suggests an oxidative addition of the epoxide to the Ir(I) complex at the



L = PMe_3

22

least substituted C-O bond. β-H elimination of the dipolar intermediate **23** or metallooxetane **24** follows to yield the observed cis-hydrido-alkyliridium (III) complexes (Figure 1.6). In addition, the formation of **25** from the reaction of **18** and β,β-dideuteriostyrene oxide (eq. 5) supports this mechanism.



L = PMe_3 (5)

25

Several Rh(I) complexes, such as $[Rh(CO)_2Cl]_2$, $RhCl(PPh_3)_3$, and $RhCl(CO)(PPh_3)_2$ have been shown to act as catalysts and convert epoxides to aldehydes or ketones. Rhodium(I) catalysts which function as Lewis

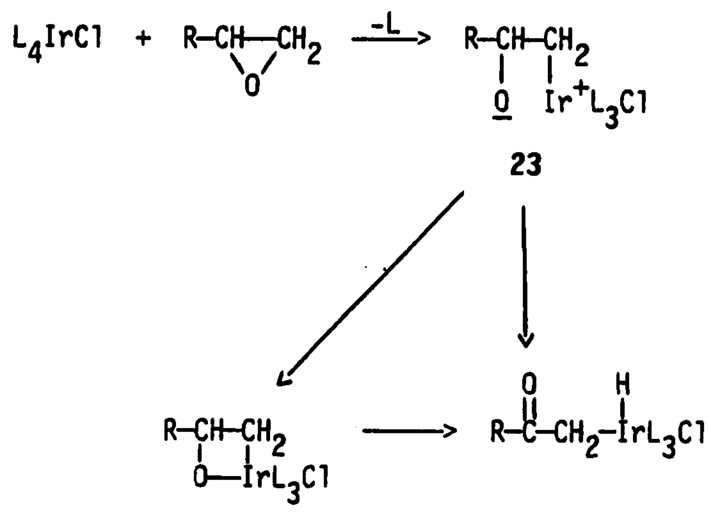
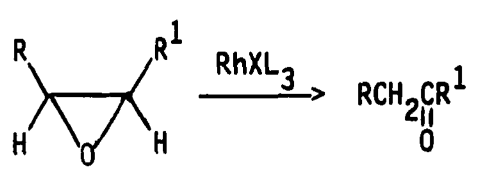


Figure 1.6. The sequence of the reactions between epoxides and Ir(I) complexes, 18

acids, for example $Rh_2(CO)_4Cl_2$, transform disubstituted epoxides mainly to aldehydes rather than ketones [18]. Initial coordination of the metal to the epoxide oxygen is proposed to give a carbonium ion intermediate **26** as shown in Figure 1.7. The relative reaction rates of epoxides in the presence of $[RhCl(CO)_2]_2$ (styrene oxide > 3,4-epoxy-3-methyl-1-butene > 3,4-epoxy-2-methyl-1-butene > 3,4-epoxy-1-butene) suggest that the reaction intermediate has carbonium ion character and this mechanism is clearly related to the Lewis acid catalyzed [19] rearrangement of epoxides to ketones or aldehydes. Ring opening of **26** gives the dipolar intermediate **27** and then migration of the most electron-releasing group generates an aldehyde.

Other Rh(I) complexes, e.g., $RhCl(PPh_3)_3$, $RhBr(PPh_3)_3$, and $RhCl(CO)(PPh_3)_2$ which do not act as acids catalyze the selective rearrangement of disubstituted oxiranes to ketones (eq. 6) [20]. The



(6)

first step in the $RhCl(PPh_3)_3$ catalyzed rearrangement is proposed to be the formation of the 14-electron complex $RhCl(PPh_3)_2$ by dissociation of PPh_3. At 170-220°C in the presence of an epoxide, dissociation is fast and complete. The liberated PPh_3 is removed continuously as $O{=}PPh_3$ which is detected (eq. 7). Addition of about one equivalent of triphenylphosphine lowers the reaction rate by 44%, but further addition of PPh_3

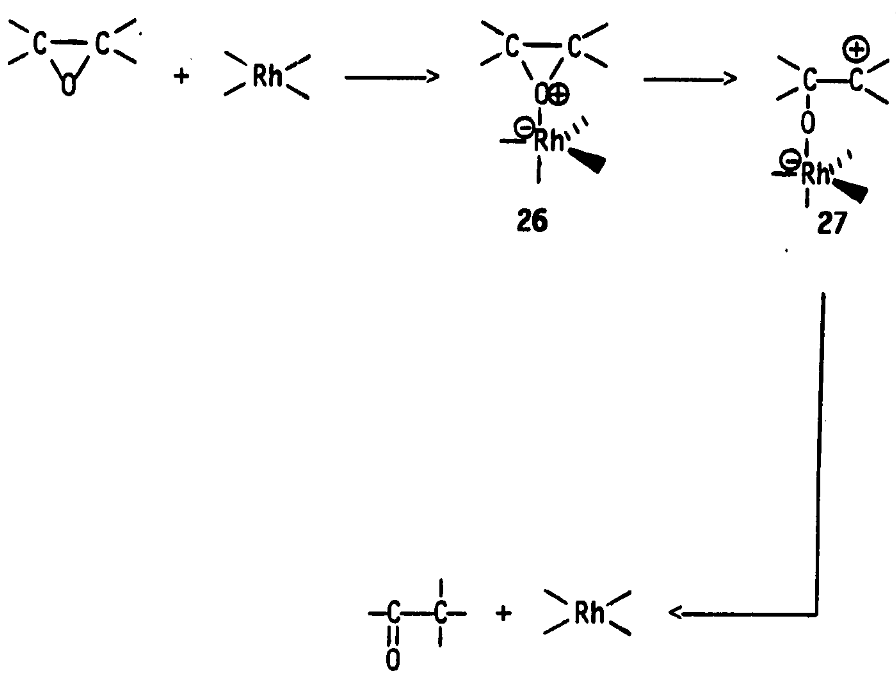
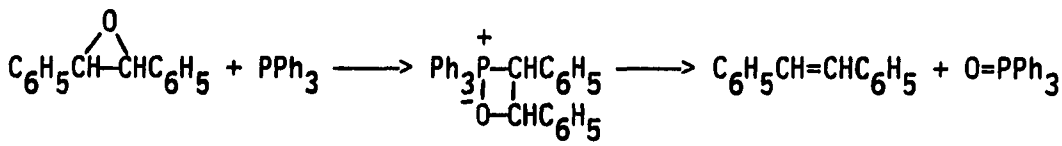


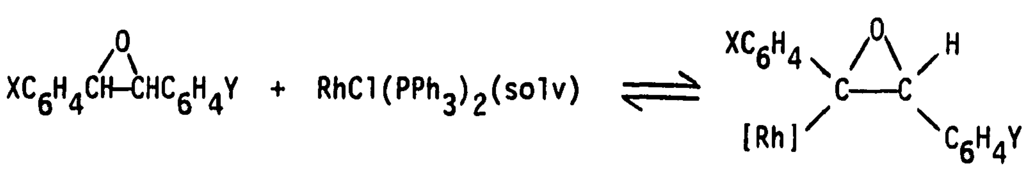
Figure 1.7. The Lewis acid, e.g., $[RhCl(CO)_2]_2$, catalyzed rearrangement of epoxides



(7)

has no effect on the rate. In the presence of a large excess of 1-methylnaphthalene (solvent), the bis(phosphine) complex has been proven to be solvated, $RhCl(PPh_3)_2(solv)$. Therefore, the active catalyst is the solvate $RhCl(PPh_3)_2(solv)$ where "solv" may represent a coordinated epoxide. Unlike Lewis acid catalyst $[RhCl(CO)_2]_2$, which transforms disubstituted epoxides to aldehydes, $RhCl(PPh_3)_3$ and the active solvated $RhCl(PPh_3)_2(solv)$ convert disubstituted epoxides to ketones.

The most probable mechanism for $RhCl(PPh_3)_3$ involves oxidative addition of an oxirane C-H bond to the rhodium catalyst. In this mechanism, the epoxide is activated by reversible nucleophilic attack of the rhodium at the oxirane carbon atom having the lowest electron density as in **28** (eq. 8). Intermediate **28** is assumed to undergo a slow



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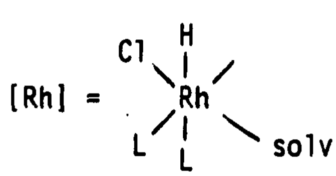
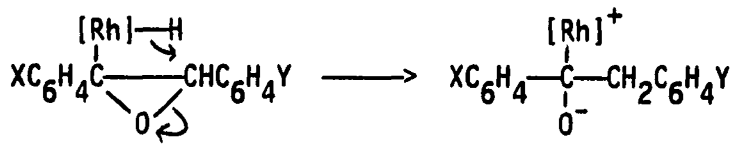


intramolecular β-hydride transfer from the metal to yield a dipolar intermediate **29** (eq. 9). The kinetic isotope effect (k_H/k_D = 1.93) is



(9)

28 **29**

typical for hydride transfer reactions [21]. In the final step, **29** undergoes reductive elimination yielding the active Rh(I) catalyst and the ketone. The complete catalytic cycle for the rearrangement of epoxides to ketones is summarized as follows (Figure 1.8): (a) fast dissociation of $RhCl(PPh_3)_3$ to the active catalyst $RhCl(PPh_3)_2$(solv), (b) fast oxidative cis addition of the epoxide to the active catalyst $RhCl(PPh_3)_2$(solv) to give **28**, (c) slow intramolecular hydride transfer **28** → **29**, (d) formation of the product and active catalyst by reductive elimination.

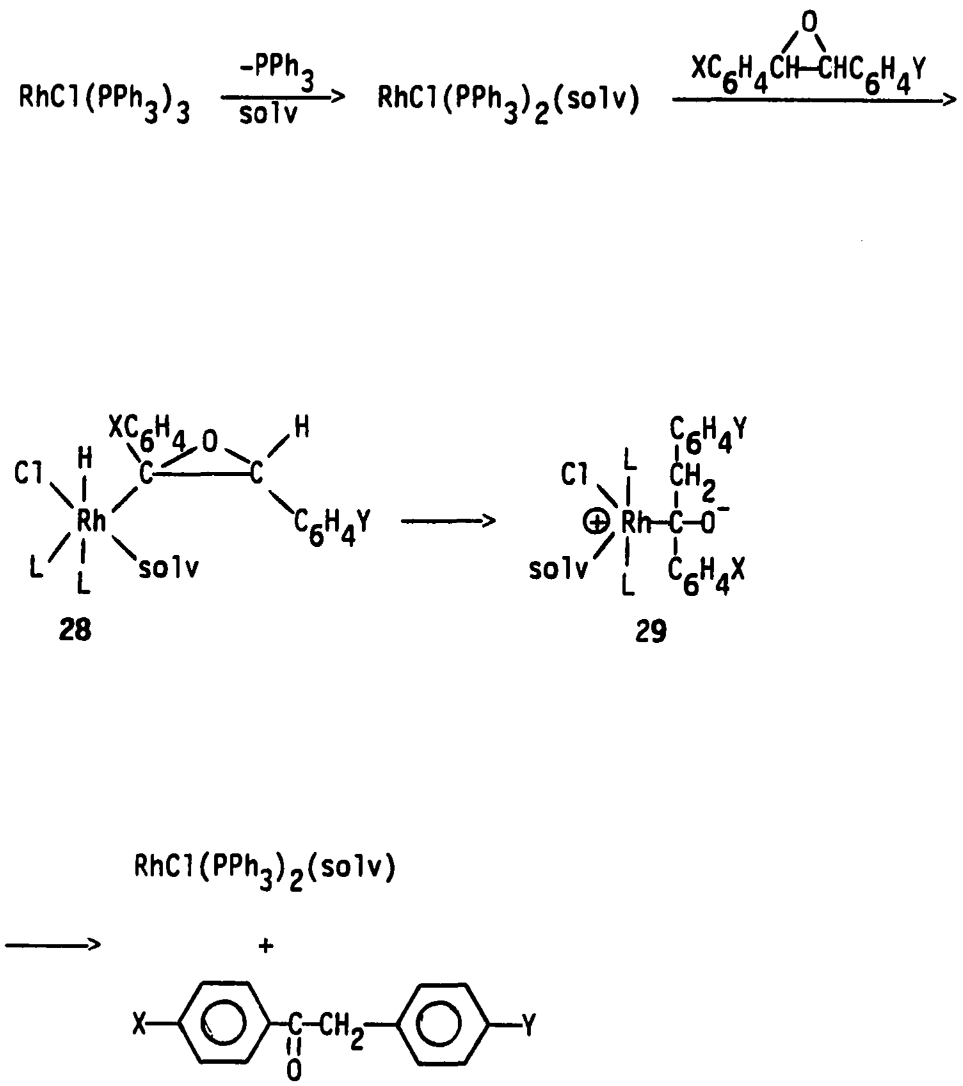
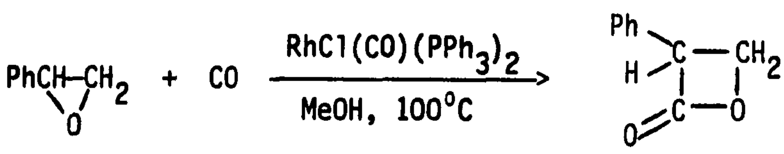


Figure 1.8. The catalytic cycle for the rearrangement of epoxides to ketones by $RhCl(PPh_3)_3$

CARBONYLATION

The Rh(I) complex, trans-carbonylchlorobis(triphenylphosphine) rhodium(I), catalyzes the carbonylation of epoxide in MeOH at 100°C yielding 67% of β-lactone (eq. 10) [22]. Two paths are proposed for



(10)

β-lactone formation. Figure 1.9 shows the Rh catalyst acting as a Lewis acid toward the epoxide oxygen. C-O bond cleavage followed by CO addition generates the dipolar intermediate **31.** By reductive elimination, β-lactone is obtained along with $RhCl(CO)(PPh_3)_2$ to complete the catalytic cycle.

Another possible route is shown in Figure 1.10; here the oxidative addition of Rh(I) to the epoxide C-O bond produces **33.** Formation of the β-lactone is achieved by CO insertion into the Rh-O bond followed by reductive elimination.

However, $Co_2(CO)_8$ [23], $K_2Fe(CO)_4$ [24], and $HCo(CO)_4$ [25] catalyze carbonylation of ethylene oxide and MeOH to afford the corresponding hydroxyester. Ethylene oxide reacts with $HCo(CO)_4$ and CO (3000 psi) in MeOH at 64°C to give methyl-3-hydroxypropionate (eq. 11) in 55% yield; propylene oxide, styrene oxide and isobutylene oxide react similarly [25]. Ethylene oxide in ether solution under 1 atm of carbon monoxide reacts rapidly with the cobalt hydridocarbonyl at 0°C yielding

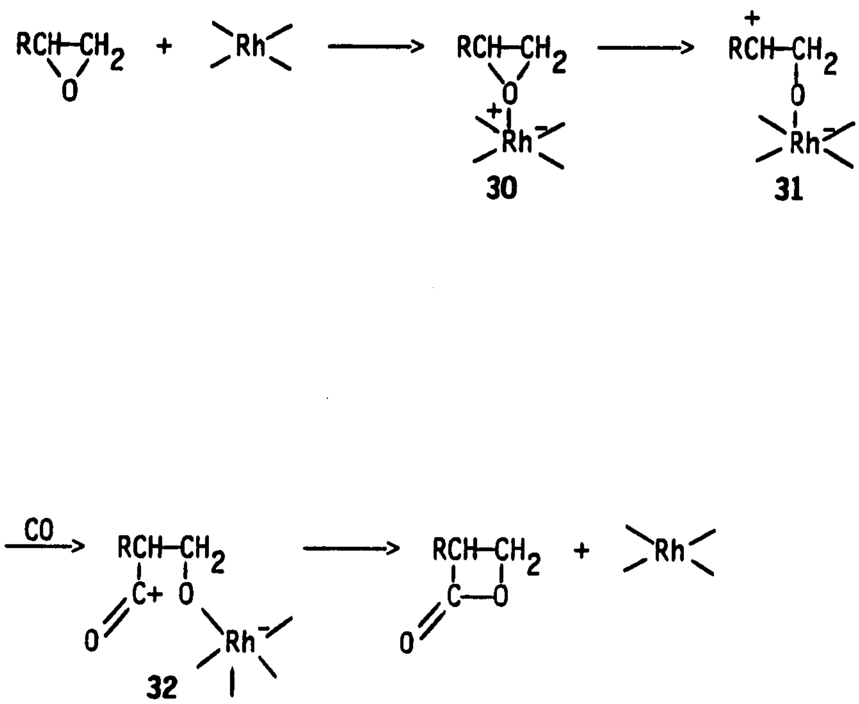


Figure 1.9. $RhCl(CO)(PPh_3)_2$ acting as Lewis acid catalyst for β-lactone formation

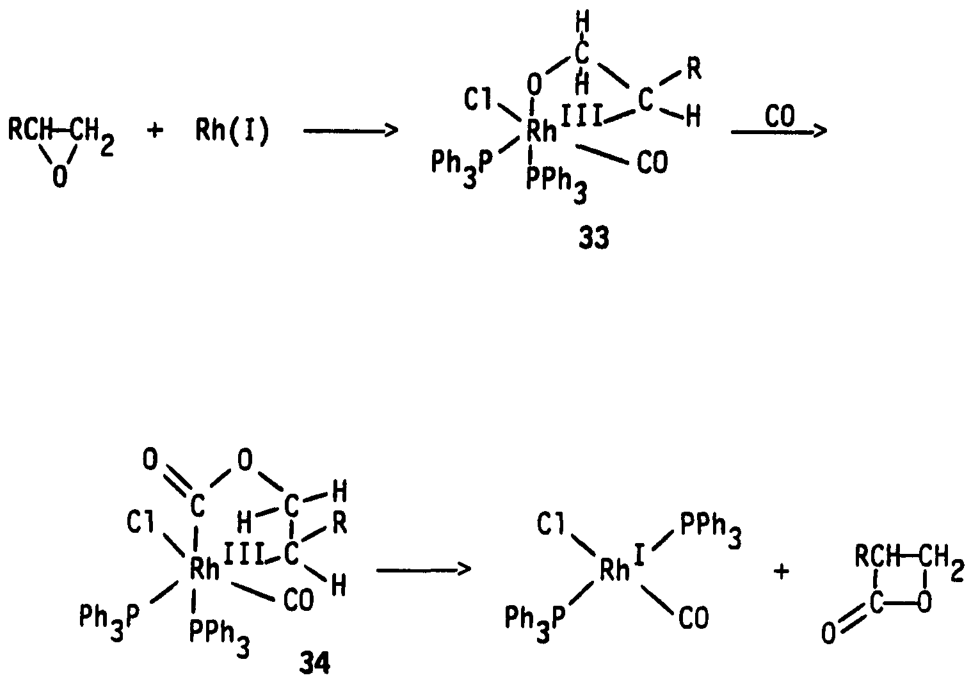


Figure 1.10. $RhCl(PPh_3)_2(CO)$ catalyze β-lactone formation through oxidative addition of epoxide C-O bond

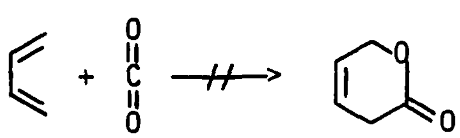
$$H_2C\overset{O}{\triangle}CH_2 + CO + CH_3OH \xrightarrow[65^\circ C]{HCo(CO)_4} HOCH_2CH_2COOCH_3 \quad (11)$$

3-hydroxypropionyl-cobalt tetracarbonyl (eq. 12). The structure of this product was confirmed by its IR spectrum and by isolation of the complex

$$CO + H_2C\overset{O}{\triangle}CH_2 + HCo(CO)_4 \xrightarrow[0^\circ C]{ether} HOCH_2CH_2COCo(CO)_4 \quad (12)$$

as the triphenylphosphine derivative, $HOCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_3(PPh_3)$. The mechanism of eq. 12 has been proposed as shown in Figure 1.11.

A direct Diels-Alder reaction of CO_2 with 1,3-dienes to generate δ-lactones (eq. 13) does not occur. However, generation of δ-lactones



(13)

from 1,3-dienes can be achieved in two steps if the diene is first epoxidized and then the epoxide carbonylated in the presence of transition metal compounds. The carbonylation of vinyl oxiranes to generate δ-lactones [26] is assisted by transition metal complexes, e.g. $Fe(CO)_5$, $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ (eq. 14). The light induced complexation of vinyl oxiranes by $Fe(CO)_5$ generates π-allyl complexes **35**; carbonylation of

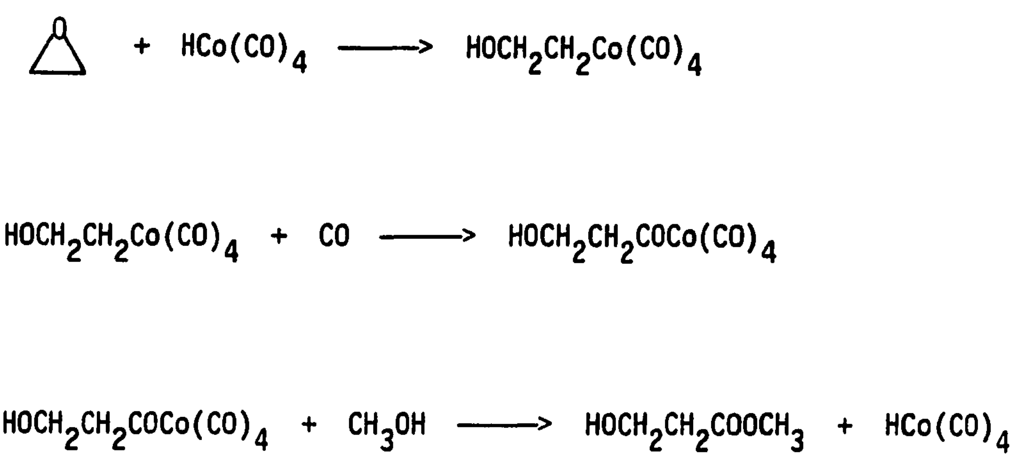
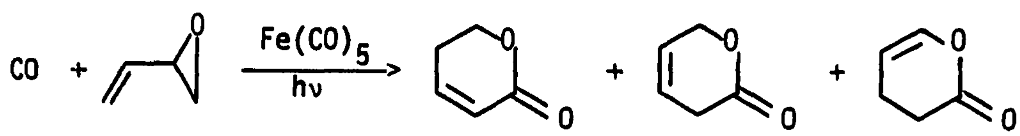
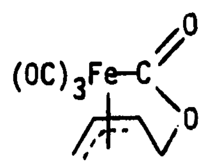


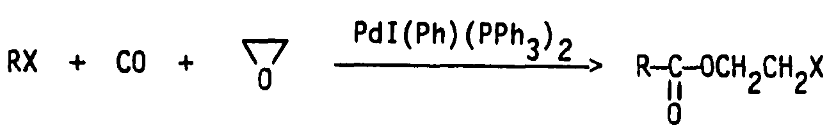
Figure 1.11. The proposed mechanism of formation of hydroxyester by $HCo(CO)_4$


(14)

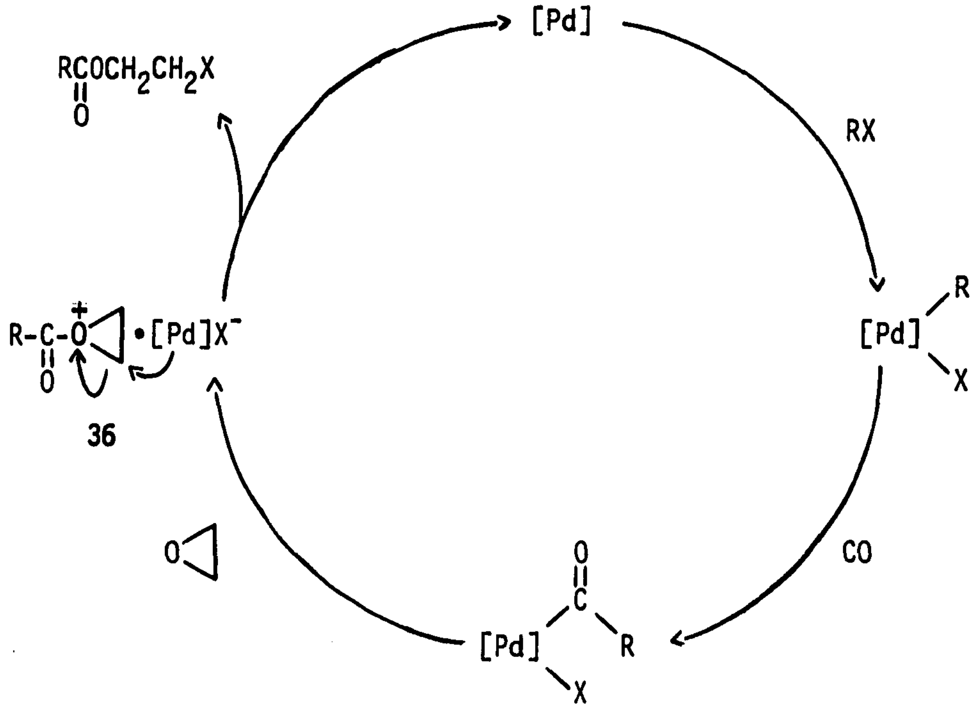
these complexes with CO gas in MeOH gives good yields (65 ~ 99%) of the unsaturated δ-lactones.


35

The synthesis of halohydrin esters is accomplished via palladium complex-catalyzed carbonylation of organic halides in the presence of epoxides (eq. 15) [27]. The reaction was carried out in an autoclave


(15)

with 20 atm of CO gas under stirring at 130°C, and the resulting halohydrin ester was obtained by distillation (42 ~ 75%). The proposed mechanism is shown in Fig. 1.12. The acyloxonium ion **36** is postulated as



[Pd] = $PdI(Ph)(PPh_3)_2$

Figurew 1.12. The proposed mechanism for halohydrin ester synthesis by $PdI(Ph)(PPh_3)_2$

an intermediate; the same type of intermediate was proposed earlier in other reactions, such as the group VI metal carbonyl-catalyzed acylative cleavage of esters by acid chlorides [28].

CONCLUSION

The foregoing section summarizes the literature in the field of the deoxygenation, rearrangement and carbonylation of epoxides induced by transition metal complexes. Epoxides are very important starting materials which convert to some useful organic compounds. It might be anticipated that other transition metal catalyzed reactions of epoxides are possible. Some of these possibilities were examined in the course of the studies reported in this dissertation.

REFERENCES

1. Wurtz, A. Ann. 1859, 110, 125; Ann. Chim. Phys. 1859, 55, 433.

2. U.S. Pat. 1,998,878 (Apr. 23, 1935), Lefort, T. E. (to Carbide and Carbon Chemicals Corp.); reissued as U.S. Pats. 20,370 (May 18, 1937), 22,241 (Dec. 29, 1942).

3. "Encyclopedia of Chemical Technology," 3rd ed.; John Wiley & Sons: New York, 1980; vol. 9, p 432.

4. Winstein, S.; Henderson, R. B. "Heterocyclic Compounds"; Elderfield, R. C. ed.; John Wiley & Sons: New York; 1950, vol. 1, p 1.

5. Young, D. W. in "Protective Groups in Organic Chemistry"; McOmie, J. F. Ed.; Plenum Press: London, 1975; Chapter 8.

6. Kochi, J. K.; Singleton, D. M.; Andrews, L. J. Tetrahedron 1968, 6 3503.

7. McMurry, J. E.; Silverstri, M. G.; Fleming, M. P.; Hoz, T.; Grayston, M. W. J. Org. Chem. 1978, 43, 3249.

8. Fujiwara, Y.; Ishikawa, R.; Akiyama, F.; Teranishi, S. J. Org. Chem. 1978, 43, 2477.

9. Hayasi, Y.; Schwartz, J. Inorg. Chem. 1981, 20, 3473.

10. Gering, W. P.; Rosenblum, M.; Tancrede, J. J. Am. Chem. Soc. 1972, 94, 7170.

11. Rosenblum, M.; Saidi, M. R.; Modhavarao, M. Tetrahedron Lett. 1975, 4009.

12. Dowd, P.; Kang, K. J. Chem. Soc., Chem. Commun. 1974, 384.

13. Alper, H.; Pes Roches, D.; Durst, T.; Legault, R. J. Org. Chem. 1976, 41, 3611.

14. Alper, H. J. Organomet. Chem. 1975, 84, 347.

15. Kobayashi, T.; Nitta, M. Chem. Lett. 1982, 325.

16. Alper, H.; Rochers, D. D. Tetrahedron Lett. 1977, 4155.

17. (a) Milstein, D.; Calabrese, J. C. J. Am. Chem. Soc. 1982, 104, 3773. (b) Milso, D. Acc. Chem. Res. 1984, 17, 221.

18. Adames, G.; Bibby, C.; Grigg, R. J. Chem. Soc., Chem. Commun. 1972, 491.

19. Grigg, R.; Shelton, G. Chem. Commun. 1971, 1248.

20. (a) Milstein, D.; Buchman, O.; Blum, J. Tetrahedron Lett. 1974, 2757. (b) Milstein, D.; Buchman, O.; Blum, J. J. Org. Chem. 1977, 42, 2299.

21. Swain, C. G.; Wiles, R. A.; Bader, B. F. W. J. Am. Chem. Soc. 1961, 83, 1945.

22. Kamiya, Y.; Kawato, K.; Ohta, H. Chem. Lett. 1980, 1549.

23. Eisenmann, J. L.; Yamartino, I. L.; Howard Jr., J. F. J. Org. Chem. 1961, 26, 2102.

24. Takegami, Y.; Watanabe, Y.; Mitsudo, T.; Masada, H. Bull. Chem. Soc. Jpn. 1968, 41, 158.

25. Heck, R. F. J. Am. Chem. Soc. 1963, 85, 1460.

26. Aumann, R.; Ring, H.; Krüger, C.; Goddard, R. Chem. Ber. 1979, 112, 3644.

27. Tanaka, M.; Koyanagi, M.; Kobayashi, T. Tetrahedron Lett. 1981, 22, 3875.

28. Alper, H.; Huang, C. C. J. Org. Chem. 1973, 38, 64.

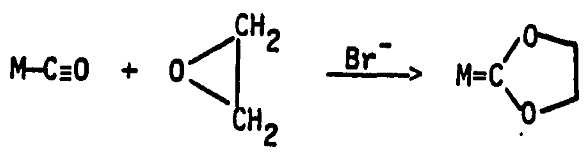
SECTION II. SYNTHESIS, STRUCTURE, AND CATALYTIC REACTIONS OF DIOXYCARBENE COMPLEXES OF IRON AND OSMIUM

ABSTRACT

$Os_3(CO)_{12}$ reacts with ethylene oxide in the presence of Br^- to give two of the few known dioxycarbene cluster compounds, $Os_3(CO)_{11}$-$(=\overline{COCH_2CH_2O})$, I, and $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II. The structure of II, established by X-ray diffraction studies, shows the dioxycarbene ligands to be in terminal, equatorial positions. Investigations of reactions of the dioxycarbene ligand showed that $Fe(CO)_4(=\overline{COCH_2CH_2O})$, III, decomposes with evolution of CO_2 and ethylene, but reacts with oxidizing agents, Me_3NO or O_2, to produce ethylene carbonate. The reaction of III with H_2 gas gives 1,3-dioxolane. In exploratory studies, ethylene oxide, CO and H_2 in the presence of Pt, Pd and Rh catalysts were found to give 1,4-dioxane, 2-methyl-1,3-dioxolane and 2-ethyl-1,3-dioxolane.

INTRODUCTION

Our group has recently synthesized a number of transition metal cyclic dioxycarbene complexes by the halide-catalyzed reaction of metal carbonyls [1-4] with ethylene oxide according to eq. 1.



(1)

M = $CpFe(CO)_2^+$, $CpRu(CO)_2^+$, $CpMn(CO)(NO)^+$, $CpFe(CO)(PPh_3)^+$, $Mn(CO)_4X$ (X = Cl, Br, I), $Re(CO)_4X$ (X = Cl, Br, I), $Fe(CO)_4$, $Mn_2(CO)_9$, $Re_2(CO)_9$

In this paper, we describe the synthesis of dioxycarbene complexes derived from $Os_3(CO)_{12}$ and an X-ray structural determination of one of them. Also, various reactions of the dioxycarbene ligand in $Fe(CO)_4$-($=\overline{COCH_2CH_2O}$) are examined, and attempts to catalyze reactions of ethylene oxide, H_2 and CO are reported.

EXPERIMENTAL

General methods

All reactions were performed under prepurified N_2. Unless noted otherwise, reagent grade chemicals were used without further purification. Methylene chloride, hexanes and acetonitrile were distilled from CaH_2 and stored under N_2 over type 4 Å molecular sieves. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2.

The starting compound $Os_3(CO)_{12}$ was prepared from OsO_4 by a modification of a literature procedure [5]. The compound $Fe(CO)_4(=\overline{COCH_2CH_2O})$ was synthesized from $Fe(CO)_5$ and ethylene oxide [4]. Trimethylamine oxide was purified by sublimation at 70 °C in vacuum. The catalysts (10% Pd/C, 10% Pt/C, 5% Rh/C, 10% Pd/Al_2O_3 and $PdCl_2$) were obtained from commercial sources. High pressure reactions were carried out in a 300 ml stainless steel pressure autoclave (Parr, model no. 4761).

Infrared spectra were recorded on Perkin-Elmer 681 instrument. ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer. ^{13}C NMR spectra were recorded at -20°C on a JEOL FX-90Q or Bruker WM-300 spectrometer; $Cr(acac)_3$ (0.1 M) was added to reduce ^{13}C data collection times. Melting points (uncorrected) of the compounds were determined in air on a Thomas hot-stage apparatus. GC-mass spectra were obtained on a Finnigan 4000 GC/MS instrument; FAB spectra of compounds I and II were obtained on a Kratos MS 50.

Synthesis of $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$, I

To a mixture of 0.15 g (1.4 mmol) of NaBr in 1 ml of $BrCH_2CH_2OH$ and 25 ml of ethylene oxide at 0°C was added 0.12 g (0.13 mmol) of $Os_3(CO)_{12}$. The mixture was stirred at 0°C for 3 days. When the reaction was complete (IR evidence), the solution was taken to dryness in vacuum. The crude compound was extracted with CH_2Cl_2, and the CH_2Cl_2 solution was filtered and chromatographed on a silica gel column (2.5 x 20 cm) using 1:2 CH_2Cl_2/hexanes as the eluent. The solvent was removed under vacuum from the yellow band eluting from the column. The residue was dissolved in CH_2Cl_2, and yellow needle crystals of the product were obtained from CH_2Cl_2/hexanes at -20°C. Yield: 0.094 g, 73%; M.p. (dec.) 92-94°C. Anal. Calcd. for $Os_3C_{14}H_4O_{13}$: C, 17.67; H, 0.42. Found: C, 17.57; H, 0.45. IR(CH_2Cl_2) ν (CO): 2119 (m), 2062 (s), 2051 (sh), 2036 (vs), 2010 (sh), 2001 (m), 1991 (s), 1970 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.66 (s, OCH_2). ^{13}C NMR (CD_2Cl_2) at -20 °C: δ 212.15 (carbene C), 189.35, 189.17, 184.57, and 184.36 (CO), 71.10 (OCH_2) ppm. Mass spectrum: m/e 951.9 (parent ion).

Synthesis of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

To a cooled mixture (0°C) of 1.0 g (9.9 mmol) of NaBr and 5 ml of $BrCH_2CH_2OH$ in a pressure autoclave previously purged with N_2 was added 1.0 g (1.11 mmol) of $Os_3(CO)_{12}$. While stirring the mixture with a magnetic stirring bar, 30 ml of ethylene oxide was introduced. After closing the autoclave, its contents were stirred at room temperature for 52 h. Then, the pressure was released and the autoclave was opened.

Unreacted ethylene oxide was evaporated by a rapid stream of N_2. The oily residue was dissolved in CH_2Cl_2, and the solution was chromatographed on a silica gel column (2.5 x 35 cm). The first band (yellow) which was eluted with 1:2 CH_2Cl_2/hexanes contained $Os_3(CO)_{11}(\overline{COCH_2CH_2O})$. The second band (orange) was eluted with 1:1 CH_2Cl_2/hexanes and contained $Os_3(CO)_{10}$-$(=\overline{COCH_2CH_2O})_2$. The orange solution was evaporated under vacuum to yield an orange-yellow powder, which was recrystallized from CH_2Cl_2/hexanes at -20 °C. Orange needle crystals were obtained. Yield: 0.271 g of $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$, 26%; 0.381 g of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, 35%. M.p. of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$: 126°C. Anal. Calcd for $C_{16}H_8O_{14}Os_3$: C, 19.30; H, 0.80. Found: C, 19.68; H, 1.03. IR(CH_2Cl_2) ν(CO): 2099 (w), 2041 (s), 2033 (sh), 2010 (vs), 2001 (sh), 1971 (m), 1948 (mw) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.58 (s, OCH_2). ^{13}C NMR(CD_2Cl_2) at -20°C: δ 214.11 (carbene C), 191.56, 191.18, 191.04, and 186.27 (CO), 70.04 (OCH_2) ppm. Mass spectrum: m/e 995.9 (parent ion).

Reactions of $Fe(CO)_4(=\overline{COCH_2CH_2O})$, III

Decomposition of $Fe(CO)_4(=\overline{COCH_2CH_2O})$. When $Fe(CO)_4(=\overline{COCH_2CH_2O})$ in CH_2Cl_2 was stirred at room temperature for more than 1 day, decomposition to a brown precipitate (probably Fe) and $Fe(CO)_5$ was evident; presumably the other products were CO_2 and C_2H_4; the CO_2 was identified as one of the products previously [4]. When a CH_2Cl_2 solution of $Fe(CO)_4$-$(=\overline{COCH_2CH_2O})$ was injected into the Finnigan GC-MS (injector block temperature was 250°C, and capillary column was 45°C), CO_2 and C_2H_4 were identified as the major decomposition products.

Reaction of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ with H_2. 0.25 g of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ in 5 ml of decalin was pressurized in an autoclave with 71.5 atm of H_2 gas at room temperature; it was heated to 200°C and stirred for 24 h. After the pressure was released, the IR spectrum of the reaction mixture showed that $Fe(CO)_4(=\overline{COCH_2CH_2O})$ had reacted completely, and a brown precipitate (probably Fe) had formed. A GC and GC-MS spectrum of the reaction solution showed the formation of a 27% yield of 1,3-dioxolane.

Reaction of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ with Me_3NO. To 0.12 g (0.50 mmol) of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ in 20 ml of CH_3CN at -78 °C, 0.197 g (2.5 mmol) of Me_3NO was added. The reaction mixture was allowed to stir at room temperature for 18 h. A brown precipitate was filtered from the mixture, and the solution was evaporated under vacuum. $Fe(CO)_4(NCMe)$ [6] [IR(CH_2Cl_2) ν(CO): 2050 (m), 1953 (s), 1931 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.70 ppm (s,CH_3CN)] was extracted from the residue with hexanes. The unextracted residue was ethylene carbonate (24% yield) [IR(CH_2Cl_2) ν(CO): 1810 (vs), 1778 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.51 ppm (s, OCH_2)].

Catalytic reactions of ethylene oxide, CO and H_2

The autoclave containing 2 ml (40 mmol) of ethylene oxide, 0.030 g (0.50 mmol) of NaCl, 2 ml of $ClCH_2CH_2OH$ and 0.04 mmol of catalyst was pressurized with 20.4 atm of H_2 and 20.4 atm of CO. The following heterogeneous and homogeneous catalysts were used: 10% Pd/C, 10% Pt/C, 10% Pd/Al_2O_3, 5% Rh/C, $PdCl_2$, $PdCl_2(PPh_3)_2$. The autoclave was heated with stirring at 175-190°C for 10 h. After cooling to room temperature, the pressure was released and the autoclave was opened; the reaction mixture was analyzed by capillary GC (temperature programmed to 200°C), which indicated the presence of several products. The major products of all of these catalytic reactions were 1,4-dioxane and 2-methyl-1,3-dioxolane. The yields (based on ethylene oxide) of 1,4-dioxane (17%) and 2-methyl-1,3-dioxolane (50%) in the 5% Rh/C-catalyzed reaction were determined by GC-MS using standard solutions of these compounds and t-butylbenzene as an internal standard.

CRYSTAL STRUCTURE DETERMINATION OF $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

Data collection and reduction

A crystal suitable for data collection, approximately 0.06-0.11 mm on a side, was selected, placed inside a glass capillary and mounted on a standard goniometer. All intensity data were collected at 245 K. The unit cell parameters were initially calculated using an automatic indexing procedure [7]. The observed systematic absences of $0k\ell$: $k=2n+1$, $h0\ell$: $\ell=2n+1$, and $hk0$: $h=2n+1$ indicated the space group Pbca. Final lattice constants were determined by a least squares fit to the 2θ values of 14 higher angle reflections. The intensities were corrected for Lorentz, polarization, and absorption effects (using an empirical absorption correction program [8] and includes a spherical correction with $\mu R=3.2$). Table 1 contains information pertinent to the data collection and reduction.

Structure solution and refinement

Using an osmium-osmium vector for the three-dimensional Patterson superposition, analysis revealed the appropriate positions for the osmium atoms. The remaining non-hydrogen atoms were located via alternate cycles of least squares calculations [9] and electron difference density calculations [10]. The atomic scattering factors were those found in the International Tables [11]. Positions of the hydrogen atoms were calculated assuming a C-H bond distance of 1.05 Å.

Restraints were added to the bond distances [12] due to the relatively small contribution to total scattering made by the individual

Table 1. Crystal data for $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

Empirical formula	$Os_3O_{14}C_{16}H_8$
Formula weight	994.80
Crystal system	orthorhombic
Space group	Pbca
a(Å)	15.391(4)
b(Å)	16.374(3)
c(Å)	17.911(2)
V(Å^3)	4493.(1)
Z	8
μ(MoKα)(cm^{-1})	180
ρ_{calc}(g cm^{-3})	2.94
T(K)	245
Diffractometer	SYNTEX $P2_1$
Monochromator	oriented graphite
Reflections measured	hkl, hkl
Radiation	MoKα(λ=0.71034 Å)
Scan type	ω-scan
Standard reflections[a]	1 (measured every 100)
Reflections collected	4155 collected, 1901 observed ($I>2\sigma(I)$)
Maximum 2θ (degrees)[b]	40

[a]No noticeable decay had occurred in the intensity of the standard.

[b]The maximum in 2θ was limited due to a rapid fall off of intensity as a function of sin(θ).

Table 1. Continued

Minimum 2θ (degrees)	3
Number of unique reflections	1135 ($I>2\sigma(I)$)
R_{av}[c]	0.103
Max. number of parameters refined	120
R[c]	0.054 (unrestrained = 0.051)
R_{ω}[c]	0.058 (unrestrained = 0.055)

[c] $R_{av}=\Sigma|F_o-\langle F_o\rangle|/\Sigma\langle F_o\rangle$; $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_{\omega}=[\omega(|F_o|-|F_c|)^2/\Sigma\omega F_o^2]^{1/2}$. $\omega=\sigma^{-2}(F_o)$.

Table 2. Atom coordinates (fractional x 10^4) and equivalent isotropic thermal parameters[a] ($Å^2$ x 10^3) in $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

Atom	x	y	z	U
Os1	3467.(1)[b]	508.(1)	1921.(1)	54.[c]
Os2	2809.(1)	-247.(1)	581.(1)	53.[c]
Os3	2152.(1)	1312.(1)	1064.(1)	52.[c]
O11	4559.(27)	-889.(22)	2536.(28)	90.[c]
O12	1947.(27)	74.(30)	2940.(24)	113.[c]
O13	5054.(22)	988.(25)	1002.(23)	84.[c]
O21	4141.(22)	-1612.(22)	487.(22)	77.[c]
O22	1412.(36)	-537.(36)	-593.(28)	148.[c]
O23	3923.(33)	776.(25)	-474.(30)	116.[c]
O24	1703.(25)	-1214.(22)	1700.(22)	86.[c]
O31	1698.(29)	2668.(25)	2152.(25)	109.[c]
O33	551.(26)	395.(30)	1570.(25)	113.[c]
O32	3647.(29)	2308.(23)	450.(24)	97.[c]
C10	3730.(27)	1386.(30)	2585.(30)	55.(14)[d]
O101	4448.(25)	1927.(27)	2544.(34)	108.(15)[d]

[a] $U = 1/3\ \Sigma\ U_{ii} \times 10^3$ where the temperature factors are defined as $\exp(-2\pi\ \Sigma\ h_i h_j a_i^* a_j^* U_{ij})$.

[b] Estimated standard deviations are given in parentheses for the least significant digit in this and all succeeding tables.

[c] Atom refined anisotropically.

[d] Atom refined isotropically.

Table 2. Continued

Atom	x	y	z	U
C101	4407.(39)	2466.(44)	3167.(47)	86.(19)[d]
C102	3513.(42)	2407.(46)	3553.(47)	93.(21)[d]
O102	3200.(25)	1709.(26)	3163.(28)	105.(14)[d]
C11	4171.(32)	-332.(36)	2309.(33)	69.(16)[d]
C12	2527.(34)	220.(39)	2540.(39)	82.(19)[d]
C13	4461.(32)	850.(31)	1385.(34)	59.(15)[d]
C21	3610.(31)	-1114.(31)	553.(32)	62.(15)[d]
C22	1976.(38)	-399.(40)	-178.(40)	90.(20)[d]
C23	3532.(46)	371.(50)	-55.(47)	112.(25)[d]
C24	2110.(37)	-836.(32)	1268.(32)	65.(15)[d]
C30	1506.(35)	1577.(34)	204.(35)	75.(17)[d]
O301	1844.(24)	1930.(24)	-456.(27)	93.(13)[d]
C301	1196.(53)	2010.(56)	-1021.(60)	131.(30)[d]
C302	379.(52)	1581.(55)	-712.(52)	116.(25)[d]
O302	641.(22)	1358.(24)	19.(25)	84.(12)[d]
C31	1870.(35)	2157.(42)	1731.(39)	84.(20)[d]
C32	3123.(36)	1895.(39)	722.(41)	84.(20)[d]
C33	1201.(32)	681.(31)	1371.(32)	56.(15)[d]

carbon atoms in the presence of osmium and the large absorption effect due to the latter element ($d_{Os=C}$=1.64-2.04 Å, $d_{C=O}$=1.10-1.44 Å prior to adding restraints). Analytical scattering factors were those found in the International Tables [13]. The "ideal" standard deviation for bonded distances was set at 0.0133; the actual value was 0.0061 indicating a proper choice of restraint targets.

Accurate standard deviations were not possible to obtain from RESLSQ since a sparse normal equations matrix is used. The values reported throughout this paper were obtained from the full-matrix routine in ALLS, by inverting the normal equations matrix for atoms with the positions from RESLSQ, and thus they represent the maximum value for the standard deviations of the parameters.

RESULTS AND DISCUSSION

Synthesis of $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$, I and $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

Since $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$[4] and $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}CPh)[=C(OMe)_2]$-[14] are the only known clusters with dioxycarbene ligands, we explored the possibility that our previous method (eq. 1) of preparing cyclic dioxycarbene complexes from metal carbonyls could be extended to $Os_3(CO)_{12}$. Indeed, $Os_3(CO)_{12}$ reacts with ethylene oxide in the presence of Br^- (eq 2) to form the mono, I, and bis, II, carbene products. The

$$Os_3(CO)_{12} + \overline{O\triangleleft} \xrightarrow{BrCH_2CH_2OH,NaBr} \underset{\text{I}}{Os_3(CO)_{11}(=\overline{COCH_2CH_2O})} + \underset{\text{II}}{Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2} \quad (2)$$

preparations of I and II were performed under a variety of conditions (Table 3); no $Os_3(CO)_{12}$ remained unreacted in any of the reactions. At 0°C, the reaction gives only I (after 3 days); however, at 25°C and 100°C, both I and II are produced which suggests that $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ is produced by a further reaction of ethylene oxide with $Os_3(CO)_{11}$-$(=\overline{COCH_2CH_2O})$. Yields of both I and II are low when the reaction is run at high temperature (100°C). This is presumably due to decomposition of the products at this temperature; in fact, the decomposition temperatures of the I and II solids are 92°C and 120°C, respectively.

Table 3. Conditions for the preparations of I and II

Temperature	CO Pressure	Time	% Yield, I	% Yield, II
0°C	--	3 days	73%	--
25°C	34 atm	1 day	29%	trace
25°C	--	52 h	26%	35%
100°C	34 atm	1 h	14%	10%

The carbene ligands in I and II could either be in axial or equatorial positions. In other M_3 clusters whose structures have been established by X-ray diffraction, the non-carbonyl ligands are axial in $Os_3(CO)_{12-n}(NCMe)_n$ (n=1 or 2) [15] and $Ru_3(CO)_{12-n}(CNBu^t)_n$ (n=1 or 2) [16], but equatorial in $Os_3(CO)_{11}[P(OMe)_3]$ [17], $Ru_3(CO)_{11}(PPh_3)$ [18] and $Os_3(CO)_{10}$(s-trans-C_4H_6) [19]. In an attempt to establish the structures of I and II, we compare their IR spectra in the ν(CO) region with those of clusters with known structures (Table 4). Because of the large number of absorptions in the spectra of both the axial and equatorial isomers, it is not possible to assign unequivocally structures to I and II on this basis.

The two cyclic dioxycarbene groups in compound II are equivalent, as indicated by the one sharp CH_2 singlet in the ^1H NMR spectrum and singlets for the carbene and CH_2 carbons in the ^{13}C spectrum. The ^{13}C NMR spectra of I and II recorded at room temperature showed only one broad band in the carbonyl region (~180 ppm downfield from Me_4Si), indicating that the CO ligands are fluxional; however, at -20°C, four CO resonances were observed in both I and II indicating reduced fluxionality of the compounds. In $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, the carbonyl groups give rise to a sharp singlet at 204.1 ppm at room temperature in the ^{13}C NMR spectrum [4]. Thus, $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ is more fluxional than II. A similar difference in fluxionality is seen in the parent $M_3(CO)_{12}$ (M=Ru, Os) clusters where the Ru cluster shows a single CO resonance even at -100°C [20], whereas, the CO doublet in $Os_3(CO)_{12}$ does not coalesce until 70°C [21].

Table 4. IR spectra of $M_3(CO)_{12-n}L_n$ complexes

Complexes	
eq-$Ru_3(CO)_{11}(PPh_3)$[a]	2087 m, 2046 s, 2030 sh, 2023 sh, 2014 s, 1996 sh, 1986 m, 1972 sh, 1960 sh
ax-$Ru_3(CO)_{11}(CN^tBu)$[a]	2093 w, 2047 s, 2040 s, 2016 m, 1998 m, 1995 m
ax-$Os_3(CO)_{11}(NCMe)$[b]	2103 w, 2052 s, 2040 s, 2020 m, 2000 vs, 1984 sh, 1981 m, 1969 vw, 1960 vw
$Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$[a]	2119 m, 2062 s, 2051 sh, 2036 vs, 2010 sh, 2001 m, 1991 s, 1970 m
eq,eq-$Os_3(CO)_{10}$(s-trans-C_4H_6)[b]	2109 m, 2063 m, 2047 s, 2019 vs, 1994 s, 1975 m, 1942 vw
ax,ax-$Ru_3(CO)_{10}(CN^tBu)_2$[a]	2065 w, 2020 s, 2007 m, 1996 s, 1990 m, 1986 m
ax,ax-$Os_3(CO)_{10}(NCMe)_2$[b]	2077 w, 2025 sh, 2019 vs, 1982 s, 1953 m
eq,eq-$Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$[b]	2099 w, 2041 s, 2033 sh, 2010 vs, 2001 sh, 1971 m, 1948 mw

[a]In hexane.

[b]In cyclohexane.

Table 5. Selected bond angles (°) and distances (Å)[a,b] in $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

	N=1	N=2	N=3
Os(N)-Os(N+1)[c]	2.883(3)	2.877(3)	2.854(3)
Os(N)-$C_{carbene}$	1.91(5)	----	1.88(6)
Os(N-1)-Os(N)-Os(N+1)	60.19(7)	59.42(7)	60.39(7)
Os(N-1)-Os(N)-C_{ax}	84(2), 99(2)	83(2), 94(3)	94(2), 83(2)
Os(N+1)-Os(N)-C_{ax}	97(2), 89(2)	85(2), 93(2)	94(3), 83(2)
Os(N-1)-Os(N)-C_{eq}	160(2)	154(2), 97(2)	158(2)
Os(N+1)-Os(N)-C_{eq}	101(2)	155(2), 96(2)	99(2)
Os(N-1)-Os(N)-$C_{carbene}$	98(1)	----	98(2)
Os(N+1)-Os(N)-$C_{carbene}$	156(2)	----	157(2)
C_{ax}-Os(N)-C_{eq}	92(3), 87(2)	90(2), 91(3), 92(3)	91(3), 92(2)
C_{ax}-Os(N)-$C_{carbene}$	89(2), 86(2)	----	92(3), 88(2)
C_{ax}-Os(N)-C_{ax}	174(2)	177(3)	177(3)
C_{eq}-Os(N)-C_{eq}	----	109(3)	----
C_{eq}-Os(N)-$C_{carbene}$	102(2)	----	103(3)
O_{ax}-C_{ax}-Os(N)	177(6), 172(5)	175(6), 178(5)	171(6), 170(5)
O_{eq}-C_{eq}-Os(N)	175(5)	174(5), 173(6)	179(6)
$O_{carbene}$-$C_{carbene}$-Os(N)	127(4), 128(3)	----	129(4), 126 (4)

[a]For the dioxycarbene groups, O-C-O, 104(4), 105(5); C-O-C, 118(4), 108(5), 115(5), 112(5); C-C-O, 111(5), 97(6), 106(7), 103(6).

[b] All bond distances noted below were restrained to the target distances given: Os-CO, 1.88 Å; C-O, in CO groups, 1.16 Å; C-O at the carbene carbon 1.42 Å; and C-C distance in the carbene ligand, 1.54 Å. The standard deviations were all set to 0.013 Å.

[c] N refers to the cyclic permutation 1, 2, 3, (note that for N=1, "N-1" is 3; for N=3, "N+1" is 1).

Structure of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

The solid state structure of compound II determined by X-ray diffraction is shown in Fig. 1. The basic coordination geometry is that of $Os_3(CO)_{12}$ [22] with the two cyclic dioxycarbene ligands occupying two equatorial carbonyl coordination sites. Each of the Os atoms has a distorted octahedral coordination geometry. All of the carbonyl ligands are terminal and nearly linear, Os-C-O, 170-174°. The three metal atoms define a triangle with an average Os-Os bond distance of 2.871 Å; this value is very close to the mean metal-metal distance (2.877(3) Å) [22] in $Os_3(CO)_{12}$. In II, the shortest Os-Os bond (2.854(3) Å) is between Os1 and Os3, which are also the atoms that bear the cyclic dioxycarbene ligands. The shortest Os-Os distance in $Os_3(CO)_{10}(NCMe)_2$ [15] is also between the Os atoms that have the coordinated MeCN ligands. As in $Os_3(CO)_{10}$(s-trans-C_4H_6) [19] and $Os_3(CO)_{11}(P(OMe)_3)$ [17] where the non-carbonyl ligands occupy the equatorial positions, the carbene ligands in II are also equatorial. The C_3O_2 carbene rings are nearly planar with the maximum deviation from planarity being 0.068 Å.

Both of the carbene ligands in II are terminal. Bridge bonding is observed in all other previously reported cluster-bound alkylidene ($=CR_2$) complexes, e.g., $(\mu_2\text{-}CO)(\mu_2\text{-}CH_2)Os_3(CO)_{10}$ [23] and $(\mu_2\text{-}H)_2(\mu_2\text{-}CH_2)Os_3$-$(CO)_{10}$ [24] and in some trimetal clusters with the =CR(OR') ligand, e.g., $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHOMe)^-]$ [25] and $Pt_2W(CO)_6(PR_3)_2[\mu\text{-}C(OMe)(Ph)]$ [26]; however, others have a terminal =CR(OR') ligand, as in $Os_3[1\text{-}\eta^1\text{-}C(OMe)\text{-}(Me)][1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)](CO)_9$ [27,28]. Bis(alkoxy) ($=C(OR)_2$) and bis(thioalkoxy) ($=C(SR)_2$) carbene ligands are generally terminal in

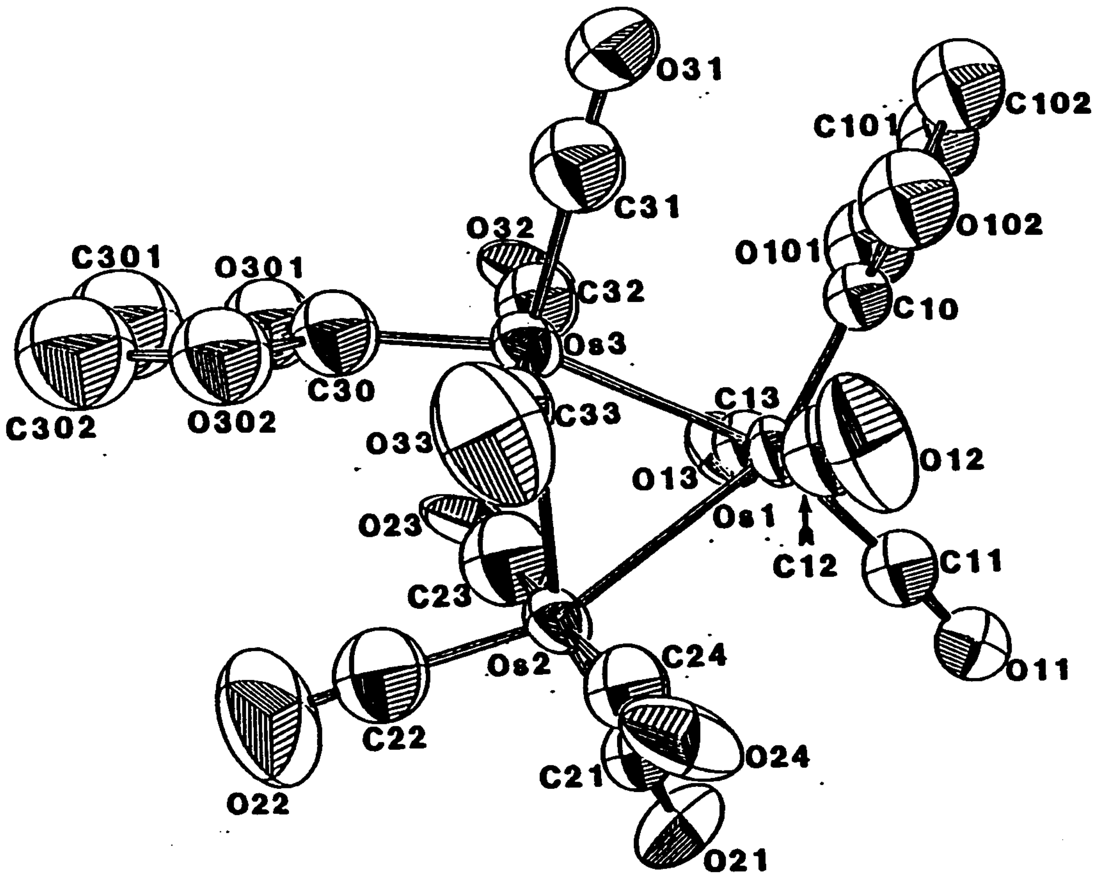


Figure 1. ORTEP drawing of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

polynuclear complexes, e.g., $(\mu_3\text{-S})_2Fe_3(CO)_8(=\overline{CSCH=CHS})$ [29], $(\mu\text{-H})Os_3(CO)_9(\eta^1\text{-C(OMe)}_2)(\mu_3\text{-CPh})$ [14] and $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ [4], but there are exceptions, e.g., $[Fe_3(CO)_9(\mu_3\text{-}\overline{CSCH_2CH_2S})(\mu_3\text{-S})]$ [30a] and others [30b].

An ORTEP [31] drawing of II in Figure 2 shows an explicit clockwise rotation for all groups of ligands when looking into the center of the osmium ring; the degrees of rotation are given in Table 6. A similar rotation is seen in other Os_3 clusters, $[Os_3(CO)_{10}(\text{trans-}CF_3(H)C{=}C(H)CF_3)(Br)]^-$ [32], $[Os_3(CO)_9(\text{trans-}CF_3(H)C{=}C(H)CF_3)(\mu\text{-Br})]^-$ [32], and $Os_3(CO)_{11}[P(OCH_3)_3]$ [17], as calculated from data in the references (entries D, E, and F in Table 6). On the other hand, there is no evidence for such a rotation in $[Os_3(CO)_{11}(NCMe)]$ [15], $[Os_3(CO)_{10}(NCMe)_2]$ [15], $H_2Os_3(CO)_{11}$ [22], and $Os_3(CO)_{12}$ [22]. It is not clear what factors lead to these rotational distortions in some Os_3 clusters and not in others.

Reactions of $Fe(CO)_4(=\overline{COCH_2CH_2O})$, III

The complex, $Fe(CO)_4(=\overline{COCH_2CH_2O})$, is not stable in CH_2Cl_2 or THF even under N_2; about 30% of it decomposes in 18 h to give $Fe(CO)_5$ and a brown precipitate which is probably Fe. Previously [4] it was noted that solid III, when heated, evolves CO_2 which was detected by the precipitation of $CaCO_3$ as the gas was passed through an aqueous solution of $Ca(OH)_2$. We have now detected both CO_2 and ethylene as products of this decomposition (eq. 3) when a CH_2Cl_2 solution of III is injected into a GC-MS

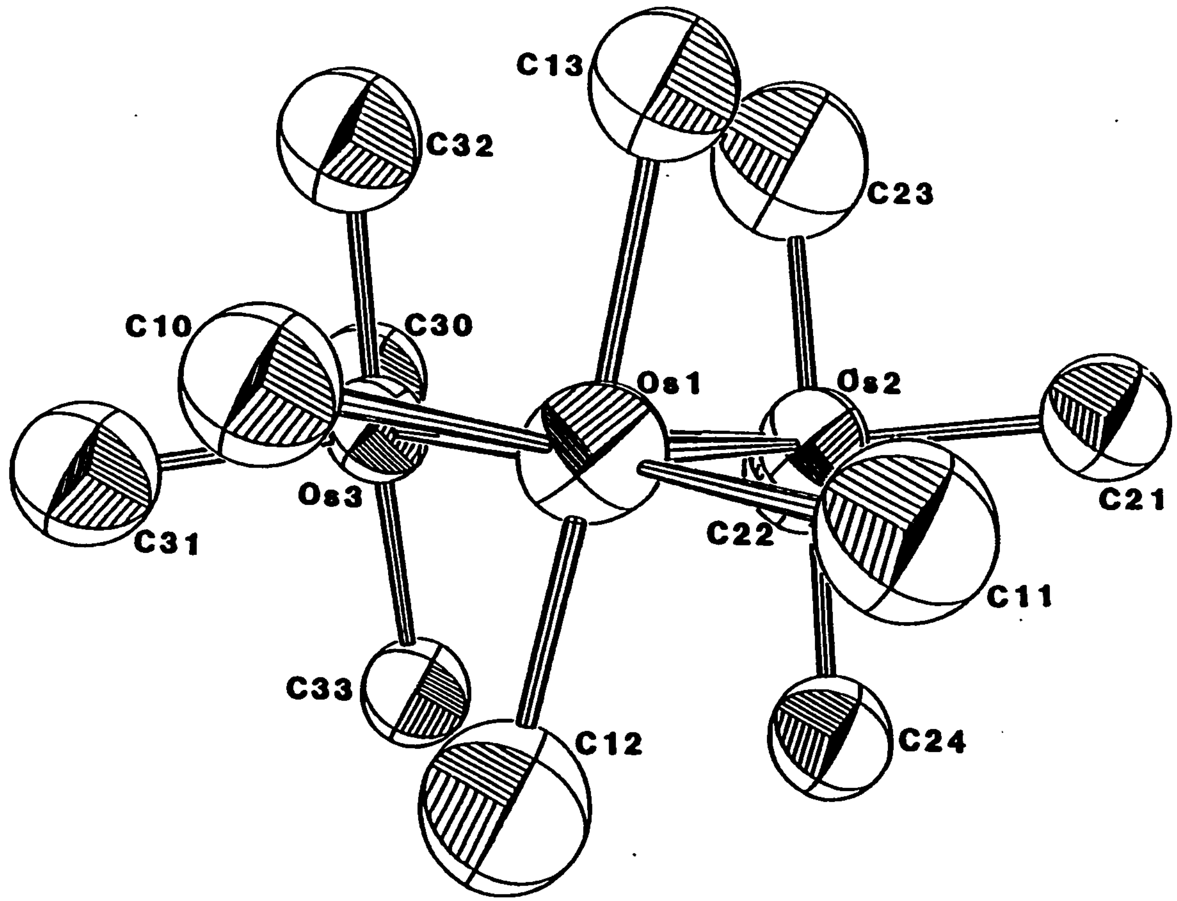


Figure 2. Perspective view of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II, showing the clockwise rotation of the ligands around the pseudo-octahedral Os atoms

Table 6. Comparison of ligand rotation[a] values in $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, II

	I	II	III	IV
A:	22.2 (C11)	6.3 (C13)	9.5 (C10)	11.3 (C12)
B:	20.4 (C22)	8.3 (C23)	7.5 (21)	8.2 (C24)
C:	25.7 (C31)	12.5 (C32)	10.0 (C30)	13.5 (C33)
D:	28.1	8.3	7.7	6.0
E:	8.4	5.9	4.3	0.9
F:	4.3,14.5,8.3	4.4,4.1,3.3	2.2,0.6,1.7	0.5,1.1,-1.0
G:	2.8,3.0,2.6	0.9,0.6,0.5	0.6,1.4,0.7	0.6.1.0,2.9
H:	-4.4,7.2,5.1	1.2,-0.9,-0.7	-0.3,-1.3,0.5	-0.8,2.2,2.4
I:	5.9,5.2,-0.8	4.0,0.5,0.3	2.8,3.4,-0.4	3.7,3.1,0.4
J:	7.6 1.2,2.6	2.8,1.6,-0.6	5.8,1.2,0.5	5.7,-0.1,2.5

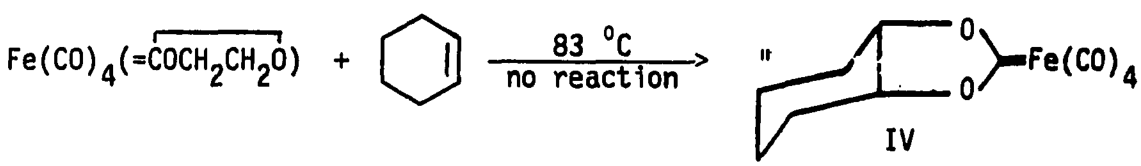
I: Vector in plane of osmium atoms, arbitrary reference of 0°.
II: Vector perpendicular to plane, 90° anticlockwise rotation.
III: Vector in plane, 180° rotation.
IV: Vector perpendicular to plane, 90° clockwise rotation.

A,B,C: Atoms on Os1, Os2, and Os3, this structure.
D: Atoms on Os3 in $[Os_3(CO)_{10}(trans\text{-}CF_3(H)C{=}C(H)CF_3)Br]^-$ in [32].
E: Atoms on Os_3 in $[Os_3(CO)_9(trans\text{-}CF_3(H)C{=}C(H)CF_3)(\mu\text{-}Br)]^-$ in [32]. The structure was inverted to give the clockwise rotation of the other structures.
F: Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{11}[P(OCH_3)_3]$ in [17].
G: Atoms on Os1, Os2, and Os3 in $H_2Os_3(CO)_{11}$ in [22].
H: Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{12}$ in [22].
I: Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{11}(NCMe)$ in [15].
J: Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{10}(NCMe)_2$ in [15].

[a]Rotation values in degrees rotated from the vectors parallel and perpendicular to the metal atoms plane as given by the headings I, II, III, and IV.

$$Fe(CO)_4(=\overline{COCH_2CH_2O}) \xrightarrow{CH_2Cl_2} CO_2 + C_2H_4 + Fe(CO)_5 + Fe + \ldots \qquad (3)$$

instrument. It is not known whether or not the free carbene $:\overline{COCH_2CH_2O}$ is an intermediate in this reaction; however, this carbene, previously suggested [33] as an intermediate in the decomposition of the nonbornadienone ketal, decomposes to CO_2 and C_2H_4. We considered the possibility that decomposition could occur by loss of C_2H_4 from III, leaving a CO_2 complex which might react with a different olefin to give a new dioxycarbene complex. However, refluxing (83°C) III in cyclohexene (eq 4) did not give the known stable dioxycarbene complex **IV** [34]; only

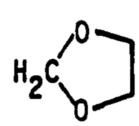


$$+ \; C_2H_4" \qquad (4)$$

decomposition of III (eq 3) occurred.

The reaction of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ with 71.5 atm of H_2 gas at 200°C in the absence of CO gave a 27% yield of 1,3-dioxolane (eq 5). However,

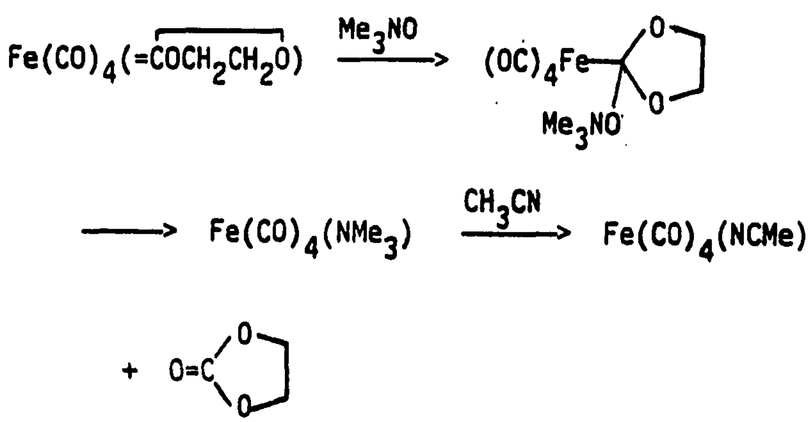
$$Fe(CO)_4(=\overline{COCH_2CH_2O}) + H_2 \xrightarrow[\text{autoclave}]{200^{\circ}C,\ \text{decalin}}$$



$$+ \; Fe \qquad (5)$$

in the presence of 34 atm of CO, this reaction did not produce any detectable 1,3-dioxolane. A possible interpretation of this result is that the initial step in the hydrogenation of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ is the loss of CO from $Fe(CO)_4(=\overline{COCH_2CH_2O})$ to give $Fe(CO)_3(=\overline{COCH_2CH_2O})$, which oxidatively adds H_2 to form an intermediate $H_2Fe(CO)_3(=\overline{COCH_2CH_2O})$ which transfers a H ligand to the carbene C and reductively eliminates 1,3-dioxolane. In this mechanism, CO inhibits the addition of H_2 and the eventual formation of 1,3-dioxolane.

The reaction of 5 equivalents of Me_3NO with $Fe(CO)_4(=\overline{COCH_2CH_2O})$ at -78°C in CH_3CN produces ethylene carbonate, $O=\overline{COCH_2CH_2O}$, in 24% yield. If only 3 equivalents of Me_3NO is used, the reaction is not complete even after one day. Also in CH_2Cl_2 solvent, the Me_3NO reaction does not go to completion. It is possible that Me_3NO oxidation of the Fe, rather than the carbene, leads to the low yield (24%) of ethylene carbonate. The formation of ethylene carbonate may occur by initial attack of Me_3NO on the carbene carbon atom as indicated by eq 6. Since a variety of other

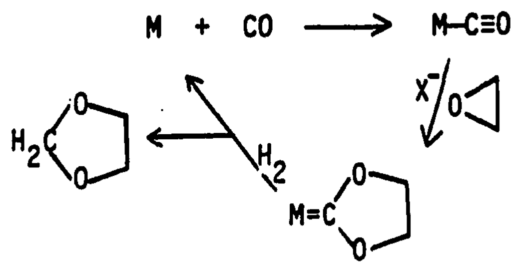


(6)

oxidizing agents including oxygen [35], pyridine N-oxide [36], dimethyl sulfoxide [37] and OH^-/Br_2 [38] have been reacted with carbene complexes to give organic products with C=O groups, several similar reactions were tried with III. Bubbling O_2 through a CH_2Cl_2 solution of $Fe(CO)_4$-($=\overline{COCH_2CH_2O}$) at room temperature for 18 h gave only a low yield of ethylene carbonate, $Fe(CO)_5$ and a brown solid. A THF solution of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ and excess $(CH_3)_2SO$ were refluxed for 4 h, but no ethylene carbonate was produced. Likewise, successive treatment of III with hydroxide and bromine in methanol did not give any of the carbonate. Ultraviolet photolysis (254 nm) of III with an equimolar amount of PPh_3 in THF gives both $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$. Similarly, refluxing I with PEt_3 in toluene gives $Os_3(CO)_{11}(PEt_3)$. Efforts to characterize the organic products formed in these reactions were not successful, but it is possible that the carbene ligand is lost as CO_2 and C_2H_4. A similar replacement of the carbene ligand was observed in reactions of $Re(CO)_4$-$(Br)(=\overline{COCH_2CH_2O})$ with bipyridine or o-phenanthroline [39].

Catalytic Reactions of Ethylene Oxide, CO and H_2

Since ethylene oxide reacts with $Fe(CO)_5$ in the presence of Br^- to form III (eq 1), and III reacts with H_2 to form 1,3-dioxolane (eq 5), it seems possible that $Fe(CO)_5$ and Br^- might catalyze the reaction of ethylene oxide, CO, and H_2 to form 1,3-dioxolane. Unfortunately, the hydrogenation step in this sequence is inhibited by CO (see above); so it appears that the $Fe(CO)_5/Br^-$ catalyst system will not be successful. However, in general, it seems possible that metals or metal complexes could catalyze the reaction of ethylene oxide, CO, and H_2 to form 1,3-dioxolane or other products derived from the dioxycarbene intermediate, III (Scheme 1). To explore this possibility, we examined several

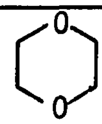
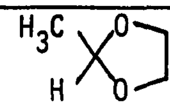


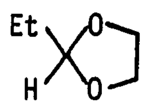
Scheme 1

reactions using a metal catalyst with NaCl in $ClCH_2CH_2OH$ solvent as shown in Table 7. In a control experiment using no metal catalyst, but all other conditions being the same as in the catalyzed reactions, a 28% yield of 1,4-dioxane was obtained, probably from the dimerization of ethylene oxide. The cyclodimerization of ethylene oxide to 1,4-dioxane is possibly catalyzed by NaCl; Cl^- attack may open the ethylene oxide ring to give the alkoxide which would add to another ethylene oxide and then cyclize to form 1,4-dioxane; it is known that halide ions promote ethylene oxide ring opening in certain organic reactions [40]. In the presence of all the metal catalysts, not only was 1,4-dioxane formation observed but also 2-methyl-1,3-dioxolane. With 10% Pt/C and $PdCl_2$, 2-ethyl-1,3-dioxolane was also identified as a product. These three were the only products that were observed in the GC-MS spectra of the reaction mixtures. In none of the reactions was 1,3-dioxolane observed as a product. It is, however,

Table 7. Reaction of ethylene oxide (40 mmol), CO (20.4 atm) and H_2 (20.4 atm) in the presence of NaCl (0.50 mmol) and catalyst (0.040 mmol) at 180°C in 2 ml of $ClCH_2CH_2OH$ for 11 h

Catalyst	Products[a]
10% Pd/C	A, B
10% Pt/C	A, B, C
10% Pd/Al_2O_3	A, B
5% Rh/C[b]	A, B
$PdCl_2$	A, B, C
$PdCl_2(PPh_3)_2$	A, B
________[c]	A

[a]A is 1,4-dioxane,  ; B is 2-methyl-1,3-dioxolane,  ;

C is 2-ethyl-1,3-dioxolane,  .

[b]The yields of A and B were 17% and 50%, respectively.

[c]The yield of A using no metal catalyst was 28%.

possible that there are other non-volatile products. It is not clear how 2-methyl-1,3-dioxolane is formed; however, it has been found [41] as a by-product in the polymerization of ethylene oxide catalyzed by $SnCl_4$ (92% dioxane and 8% 2-methyl-1,3-dioxolane are the volatile products in addition to the ethylene oxide polymer). A possible mechanism might involve isomerization of ethylene oxide to CH_3CHO, known to occur in the presence of $MnBr_2$ [42], followed by reaction with ethylene oxide to give 2-methyl-1,3-dioxolane [43]. A possible mechanism for the formation of 2-ethyl-1,3-dioxolane might proceed by the hydroformylation (H_2 and CO) [44,45] of ethylene (generated by the decomposition of ethylene oxide) to give CH_3CH_2CHO which reacts with ethylene oxide to give 2-ethyl-1,3-dioxolane [43].

Although we are not aware of other attempts to catalyze reactions of ethylene oxide, CO, and H_2, epoxides are known to be deoxygenated to olefins and CO_2 by $[Rh(CO)_2Cl]_2$ [46], $Co_2(CO)_8$ [47], $Mo(CO)_6$ [48], and $Fe(CO)_5$ [49]. Also, the reaction of ethylene oxide with CO to give β-lactones is catalyzed by $RhCl(CO)(PPh_3)_2$ [50].

Supplementary material

Listing of anisotropic thermal parameters, hydrogen atom positions, and calculated and observed structure factors (6 pages) have been deposited with the Editor-in-Chief.

Acknowledgment

This work was supported by the U.S. Department of Energy under contract no. W-7405-Eng-82, Office of Basic Energy Sciences, Chemical Sciences and Materials Sciences Divisions.

REFERENCES

1. Singh, M. M.; Angelici, R. J. Angew. Chem. Int. Ed. Engl. 1983, 22, 163; Angew. Chem. Suppl. 1983, 22, 184.

2. Singh, M. M.; Angelici, R. J. Inorg. Chem. 1984, 23, 2691.

3. Singh, M. M.; Angelici, R. J. Inorg. Chem. 1984, 23, 2699.

4. Singh, M. M.; Angelici, R. J. Inorg. Chim. Acta 1985, 100, 57.

5. Bradford, C. W.; Nyholm, R. S. Chem. Comm. 1967, 384.

6. Cotton, F. A.; Parish, R. V. J. Chem. Soc. 1960, 1440.

7. Jacobson, R. A. J. Appl. Crystallogr. 1976, 9, 115.

8. Karcher, B. A., Ph.D. Dissertation, Iowa State University, Ames, 1981.

9. Lapp, R. L.; Jacobson, R. A. "ALLS: A Generalized Crystallographic Least Squares Program", U.S. DOE Report, IS-4708; Iowa State University, Ames, IA, 1979.

10. Powell, D. R.; Jacobson, R. A. "FOUR: A Generalized Crystallographic Fourier Program", U.S. DOE Report, IS-4337; Iowa State University, Ames, IA, 1980.

11. a) Atomic Scattering Factors were obtained from: Cromer, D. T.; Weber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a, pp. 71-79; b) Hydrogen scattering factors were taken from: Steward, R. F.; Davidson, E. R.; Simpson, W. T. J. Chem. Phys. 1965, 42, 3175; c) Real and imaginary corrections for anomalous dispersion of the osmium atoms were obtained from: Cromer, D. T.; Weber, J. T. International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1, pp. 149-150.

12. Flippen-Anderson, J. L.; Gilardi, R.; Konnert, J. H. "Restrained Least-Squares Program (RESLSQ)", NRL Memorandum Report, 5042; Naval Research Lab.: Washington, D.C., 1983.

13. Analytical Scattering Factors for Os, O, C and H were obtained from: Cromer, D. T.; Weber, J. T. International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2b p. 99.

14. Shapley, J. R.; Yeh, Wen-Yam; Churchill, M. R.; Li, Yong-ji Organometallics 1985, 4, 1898.

15. Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R.; Rosales, M. J. J. Chem. Soc., Dalton Trans. 1982, 233.

16. Bruce, M. I.; Matisons, J. G.; Wallis, R. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. J. Chem. Soc., Dalton Trans. 1983, 2365.

17. Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. Acta Crystallogr. (B) 1978, 34, 666.

18. Forbes, E. J.; Goodhand, N.; Jones, D. L.; Hamor, T. A. J. Organomet. Chem. 1979, 182, 143.

19. Pierpont, C. G. Inorg. Chem. 1978, 17, 1976.

20. Aime, S.; Gambino, O.; Milone, L.; Sappa, E.; Rosenberg, E. Inorg. Chim. Acta 1975, 15, 53.

21. Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W.; Robinson, B. H.; Jackson, W. G. J. Chem. Soc., Chem. Commun. 1974, 1042.

22. Churchill, M. R.; DeBoer, B. G. Inorg. Chem. 1977, 16, 878.

23. Steinmetz, G. R.; Geoffroy, G. L. J. Am. Chem. Soc. 1981, 103, 1278.

24. Calvert, R. B.; Shapley, J. R. J. Am. Chem. Soc. 1977, 99, 5225.

25. Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. J. Am. Chem. Soc. 1983, 105, 140.

26. Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1980, 1615.

27. Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. J. Am. Chem. Soc. 1982, 104, 4679.

28. Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. J. Am. Chem. Soc. 1984, 106, 5926.

29. Benoit, A.; Le Marouille, J.-Y.; Mahé, C.; Patin, H. J. Organomet. Chem. 1982, 233, C51.

30. (a) Kruger, G. J.; Linford, L.; Raubenheimer, H. G.; Chalmers, A. A. J. Organomet. Chem. 1984, 262, 69; (b) Matachek, J. R.; Angelici, R. J. Inorg. Chem. 1986, 25, 2877.

31. Johnson, C. K. "ORTEP", Report ORNL-3794, Oak Ridge National Lab.: Oak Ridge, TN, 1965.

32. Dawoodi, Z.; Mays, M. J.; Raithby, P. R.; Hanrick, K.; Clegg, W.; Weber, G. J. Organomet. Chem. 1983, 249, 149.

33. Lemal, D. M.; Gosselink, E. P.; McGregor, S. D. J. Am. Chem. Soc. 1966, 88, 582.

34. Daub, J.; Erhardt, U.; Kappler, J.; Trautz, V. J. Organomet. Chem. 1974, 69, 423.

35. Fischer, E. O.; Riedmüller, S. Chem. Ber. 1974, 107, 915.

36. Cotton, F. A.; Lukehart, C. M. J. Am. Chem. Soc. 1971, 93, 2672.

37. Casey, C. P. in Alper, H. (ed.), "Transition Metal Organometallics in Organic Synthesis"; New York: Academic Press, 1976-1978; Vol. 1.

38. Curtis, P. J.; Davies, S. G. J. Chem. Soc., Chem. Commun. 1984, 747.

39. Miessler, G. L.; Kim, S.; Jacobson, R. A.; Angelici, R. J. Inorg. Chem. 1987, 26, 1690.

40. Rosowsky, A. in Weissberger, A. (ed.), "Heterocyclic Compounds with Three and Four Membered Rings", Part I, Interscience: New York, 1964, p. 1.

41. Worsfold, D. J.; Eastham, A. M. J. Am. Chem. Soc. 1957, 79, 897.

42. Sicedison S. P. A. (by Paolo Ciattoni). Fr. 1,318,025, Feb. 15, 1963; Ital. Appl. Jan. 27, 1961; 12 pp; Chem. Abstr. 1963, 59, PZ650h.

43. Sergeen, G. B.; Movsumzade, M. M.; Zenin, S. V.; Shabanov, A. L.; Akhmedov, S. I.; Smirnov, U. V.; Polyakov, V. A. Moscow Univ. Chem. Bull. 1975, 30, 36; Chem. Abstr. 1975, 83, 95958u.

44. Markó, L. J. Organometal. Chem. 1983, 245, 309.

45. Keim, W.; Ed., "Catalysis in C_1 Chemistry", Reidel Publishing Co.: Boston, 1983.

46. Ashworth, R. W.; Berchtold, G. A. Tetrahedron Lett. 1977, 343.

47. Dowd, P.; Kang, K. J. Chem. Soc., Chem. Commun. 1974, 384.

48. Alper, H.; Roches, D. D.; Durst, T.; Legault, R. J. Org. Chem. 1976, 41, 3611.

49. Alper, H.; Roches, D. D. Tetrahedron Lett. 1977, 4155.

50. Kamiya, Y.; Kawato, K.; Ohta, H. Chem. Lett. 1980, 1549.

SUPPLEMENTARY MATERIAL

Table S1. Hydrogen atom coordinates[a] (fractional x 10^4) for $Os_3(CO)_{10}(C_3H_4O_2)_2$, II

Atom	x	y	z
H34	4472.	3089.	2967.
H35	4877.	2243.	3602.
H36	3112.	2948.	3385.
H37	3576.	2273.	4149.
H38	1413.	1626.	-1517.
H39	1021.	2631.	-1113.
H40	-153.	2003.	-679.
H41	276.	986.	-1028.

[a]The hydrogen atom parameters were calculated and not refined; U($Å^2$ x 10^3) = 63.3.

Table S2. Anisotropic thermal parameters[a] ($Å^2 \times 10^3$) for $Os_3(CO)_{10}(C_3H_4O_2)_2$, II

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os1	74.(1)	56.(1)	33.(1)	-8.(1)	-7.(1)	0.(1)
Os2	70.(1)	50.(1)	38.(1)	-3.(1)	2.(1)	-7.(1)
Os3	65.(1)	52.(1)	39.(1)	-1.(1)	3.(1)	-3.(1)
O33	101.(30)	162.(44)	75.(34)	-17.(32)	14.(24)	-10.(38)
O32	151.(39)	72.(28)	69.(35)	-21.(25)	34.(29)	-27.(28)
O31	174.(45)	73.(31)	78.(37)	52.(27)	-13.(30)	4.(29)
O21	81.(24)	72.(25)	79.(33)	37.(20)	44.(22)	20.(25)
O23	176.(44)	67.(30)	105.(44)	-15.(27)	10.(35)	-52.(33)
O22	181.(49)	198.(57)	67.(35)	11.(42)	-24.(35)	-35.(46)
O24	116.(30)	72.(26)	69.(30)	-23.(22)	35.(24)	-35.(26)
O12	113.(31)	165.(44)	61.(31)	-28.(28)	4.(26)	-8.(32)
O11	124.(30)	64.(25)	82.(31)	4.(26)	-31.(26)	-5.(29)
O13	80.(24)	105.(32)	66.(28)	0.(21)	17.(23)	-24.(27)

[a]The form of the temperature factor is $\exp(-2\pi\Sigma\, U_{ij}h_ih_ja_i^*a_j^*)$.

Table S3. Observed and calculated structure factors for $Os_3(CO)_{10}(C_3H_4O_2)_2$, II

K	L	Fo	Fc
H = 0			
K	L	Fo	Fc
0	2	136	151
0	4	163	-187
0	6	336	-332
0	8	608	-595
0	10	225	223
0	12	245	-255
0	14	240	-266
0	16	342	356
2	0	830	851
2	1	576	-620
2	4	166	169
2	5	422	416
2	7	365	344
2	8	631	-619
2	9	338	302
2	11	497	-515
2	12	180	-173
2	13	300	-296
2	15	142	155
2	16	339	345
4	1	234	-261
4	3	363	374
4	4	497	510
4	5	393	408
4	6	194	176
4	7	273	-289
4	8	654	-663
4	9	297	301
4	10	444	-436
4	11	324	-324
4	12	131	-100
4	14	282	287
4	16	193	227
6	0	172	167
6	2	328	356
6	3	804	810
6	5	346	353
6	6	242	-263
6	7	337	-346
6	9	186	172
8	0	131	148
8	1	172	-182
8	2	318	342
8	3	363	364
8	4	308	-287
8	5	361	339
8	6	359	-365
8	8	304	304
8	11	314	-321
8	13	257	-254
8	14	102	-109
10	0	388	-412
10	2	169	164
10	5	274	265
10	7	366	381
10	8	167	180
10	10	272	-286
10	11	281	-302
10	13	261	-277
12	0	400	-433
12	1	221	289
12	3	241	252
12	4	150	146
12	5	145	157
12	9	135	-136
12	10	214	-228
14	1	273	310
14	3	166	179
14	8	173	169
H = 1			
K	L	Fo	Fc
0	2	1147	-1105
0	4	296	-291
0	6	296	-291
0	8	292	278
0	10	184	175
0	12	237	-235
0	14	405	415
0	16	164	198
1	1	129	-126
1	3	154	136
1	5	279	-275
1	7	297	283
1	9	127	130
1	13	176	155
1	15	154	-152
2	1	442	-416
2	2	607	-552
2	3	429	407
2	5	260	223
2	6	499	-460
2	9	498	-463
2	10	266	292
2	11	337	-335
2	12	140	101
2	13	331	338
2	14	381	376
2	15	117	133
3	1	284	-275
3	3	148	143
3	4	489	-460
3	7	138	127
3	11	151	-106
3	12	158	154
4	1	317	305
4	2	223	208
4	3	555	508
4	5	566	-525
4	6	734	-690
4	8	296	-311
4	9	129	-131
4	10	318	283
4	11	297	-269
4	12	424	421
4	13	194	202
4	14	251	235
5	2	130	131
5	4	219	-216
5	12	253	249
5	14	130	-104
6	1	446	463
6	2	129	-120
6	3	334	295
6	4	513	-484
6	5	770	-721
6	9	190	142
6	11	170	-173
6	12	165	145
6	15	115	-140
7	1	112	121
7	3	149	-124
7	4	231	-212
7	11	114	123
7	12	158	164
7	13	116	-101
8	1	187	203
8	2	254	-260
8	3	343	333
8	4	347	-317
8	5	134	-119
8	6	260	254
8	7	206	-194
8	8	128	102
8	9	356	-344
8	10	138	-144
8	11	276	-268
8	13	123	136
9	2	116	-121
9	3	171	-166
9	5	142	149
10	1	86	87
10	2	225	256
10	3	226	219
10	4	188	-172
10	5	187	195
10	7	242	-232
10	8	138	-150
10	9	437	-415
10	11	222	-213
10	12	226	212
11	5	154	174
12	1	309	347
12	2	310	349
12	7	205	-207
12	8	172	-164
14	1	279	310
14	3	130	-119
14	6	158	161
14	7	186	-173
H = 2			
K	L	Fo	Fc
0	0	960	-1164
0	2	338	-350
0	4	314	306
0	6	350	340
0	8	377	372
0	10	133	-146
0	12	230	224
0	14	186	158
0	16	180	-185
1	1	487	485
1	2	303	-291
1	3	185	-186
1	4	118	118
1	5	314	285
1	6	205	204
1	7	502	486
1	8	212	-195
1	9	339	-329
1	13	137	-156
1	15	213	-193
1	17	219	223
2	0	560	-577
2	1	348	341
2	2	226	-226
2	3	197	194
2	4	182	-184
2	5	142	-121
2	6	170	170
2	7	370	-345
2	8	430	444
2	9	152	-163
2	10	171	177
2	11	352	353
2	12	132	121
2	13	238	232
2	16	208	-231
3	0	175	175
3	1	285	277
3	2	361	-352
3	3	129	130
3	4	165	151
3	6	325	319
3	8	329	-316
3	9	274	-258
3	10	240	222
3	11	145	137
3	15	168	-158
3	16	124	124
4	0	118	-130
4	2	186	-178
4	3	540	-520
4	4	513	-493
4	5	120	-114
4	6	102	-19
4	8	480	470
4	10	437	434
4	11	179	162
4	14	263	-269
4	16	168	-186
5	0	549	571
5	1	196	178
5	3	308	293
5	5	140	133
5	6	231	223
5	8	181	-188
5	10	402	408
5	14	162	-182
6	0	326	-355
6	1	196	-207
6	2	194	-189
6	3	691	-649
6	5	244	-237
6	6	218	204
6	7	277	268
6	13	119	51
6	15	129	152
7	0	185	191
7	1	288	-298
7	2	317	-303
7	5	122	109
7	6	114	139
7	9	207	208
7	10	358	345
7	11	230	-217
7	14	119	-115
8	0	307	-328
8	2	158	-160
8	3	187	-178
8	4	255	243
8	5	302	-285
8	6	299	286
8	7	187	-195
8	8	178	-163
8	11	271	259
8	13	223	204
9	0	155	-178
9	1	290	-306
9	2	186	-189
9	3	107	106
9	6	201	190
9	7	157	-153
9	9	272	259
9	11	188	-151
10	0	165	187
10	1	74	40
10	5	317	-297
10	7	383	-366
10	10	155	152
10	11	292	283
10	13	235	239
11	0	216	-231
11	1	123	-154
11	3	181	175
11	7	242	-240
11	8	151	138
11	9	148	152
12	0	293	328
12	1	160	-175
12	3	256	-269
12	4	137	-154
12	5	175	-162
12	6	120	-125
12	10	135	117
13	0	109	-139
13	2	86	87

Table S3. Continued

K	L	Fo	Fc
13	4	106	-123
13	8	224	217
14	1	172	-176
14	3	218	-226
15	0	146	-169
15	1	79	-64
H = 3			
K	L	Fo	Fc
0	2	596	593
0	4	713	715
0	6	109	-96
0	8	234	-233
0	16	243	-242
1	1	193	200
1	2	217	219
1	3	133	-129
1	4	218	222
1	5	596	596
1	6	227	-221
1	7	447	-444
1	8	162	-140
1	9	381	-371
1	13	134	-159
1	15	312	328
1	16	127	-106
2	1	71	69
2	2	86	70
2	3	153	-126
2	4	622	609
2	5	424	-409
2	6	282	271
2	8	125	134
2	9	348	337
2	12	292	-283
2	14	138	-157
2	15	219	-213
2	16	118	-81
3	1	567	553
3	3	353	-336
3	4	785	764
3	6	269	-264
3	7	264	-267
3	10	140	141
3	11	145	133
3	12	180	-176
3	13	268	-246
3	16	147	-164
4	1	404	-392
4	2	161	-166
4	4	192	193
4	6	423	419
4	7	169	160
4	8	326	318
4	9	164	167
4	10	223	-202
4	12	383	-380
4	14	144	-142
5	1	295	297
5	2	367	-350
5	4	468	446
5	5	207	-200
5	7	119	-118
5	8	227	242
5	12	483	-472
6	1	362	-358
6	2	191	186
6	3	112	118
6	4	206	200
6	5	287	283
6	7	235	229
6	12	112	-62
6	13	206	179
7	1	131	-125
7	2	205	-196
7	3	306	299
7	4	378	366
7	8	200	199
7	9	192	-181
7	11	219	-225
7	12	299	-306
7	13	188	194
8	1	189	-196
8	2	354	366
8	3	129	-110
8	7	175	175
8	9	276	265
8	12	144	144
8	14	115	-72
9	1	99	-117
9	2	216	226
9	3	317	319
9	4	338	339
9	5	136	-150
9	7	108	94
9	11	195	-209
9	13	175	181
10	1	75	-63
10	3	228	-227
10	4	98	-86
10	5	150	-155
10	7	155	172
10	9	337	332
10	11	149	143
11	2	184	173
11	3	108	124
11	4	90	80
11	5	317	-313
11	6	132	119
11	7	122	109
11	9	140	126
12	1	202	-203
12	2	158	-157
12	4	163	-157
12	5	128	142
12	6	159	114
12	7	128	127
12	8	104	96
13	4	121	-100
13	6	291	264
14	1	186	-196
14	5	172	167
14	7	102	73
15	1	116	-125
15	2	110	115
H = 4			
K	L	Fo	Fc
0	2	439	457
0	4	324	-329
0	6	573	-574
0	8	210	226
0	10	159	-159
1	0	166	172
1	1	128	-139
1	4	196	-191
1	5	269	-261
1	6	234	-249
1	7	638	-609
1	8	157	155
1	9	210	216
1	11	170	167
1	13	239	261
1	14	111	-106
1	15	114	121
2	0	95	113
2	2	404	406
2	3	359	-347
2	5	142	94
2	6	291	-315
2	7	414	415
2	10	382	-376
2	11	162	-140
2	13	174	-152
3	0	102	-109
3	1	449	-434
3	2	442	436
3	3	457	-452
3	4	282	-284
3	5	194	-155
3	6	355	-339
3	8	154	156
3	9	173	162
3	15	190	205
4	0	134	-141
4	1	349	379
4	2	183	171
4	4	331	314
4	7	250	240
4	8	261	-255
4	9	270	-261
4	10	413	-414
4	14	182	188
4	15	150	-169
4	16	126	87
5	0	281	-282
5	1	207	-212
5	2	268	271
5	3	379	-386
5	4	195	204
5	5	140	-124
5	8	169	-144
5	10	419	-419
5	14	208	215
5	15	117	109
6	0	326	344
6	1	481	473
6	2	87	84
6	3	369	368
6	5	82	59
6	7	138	131
6	8	230	-210
6	9	304	-300
6	11	125	129
6	15	223	-229
7	0	133	-129
7	1	259	251
7	2	251	257
7	3	84	94
7	4	135	128
7	5	117	-120
7	6	149	-145
7	7	95	-107
7	9	186	-185
7	10	338	-336
7	11	267	263
7	14	135	128
8	0	466	476
8	1	164	170
8	3	106	105
8	4	152	-149
8	5	167	169
8	7	264	250
8	8	137	-122
8	9	188	-144
8	10	204	204
8	11	112	-84
8	13	121	-140
8	14	148	-139
9	0	314	316
9	1	248	252
9	2	193	190
9	4	162	-188
9	5	127	-135
9	6	284	-274
9	9	165	-171
9	11	128	144
10	0	192	195
10	2	149	-165
10	5	230	224
10	6	139	140
10	7	240	242
10	8	162	-161
10	11	188	-189
11	0	283	303
11	2	86	98
11	3	212	-209
11	7	220	220
11	8	175	-156
12	2	155	-160
12	3	210	206
12	4	112	115
12	5	128	130
12	6	158	148
12	8	105	-116
13	4	140	143
13	7	110	98
13	8	252	-240
14	3	214	219
15	0	140	138
15	1	79	83
H = 5			
K	L	Fo	Fc
0	2	103	-109
0	4	686	-734
0	6	338	339
0	10	151	-127
0	12	272	294
0	16	191	197
1	1	87	-91
1	2	250	-259
1	3	179	-184
1	4	87	-82
1	5	172	-168
1	6	195	196
1	7	273	282
1	8	191	183
1	9	367	389
1	11	210	193
1	12	158	-141
1	15	233	-236
2	4	533	-523
2	5	349	351
2	7	184	-178
2	8	117	-125
2	9	189	-199
2	12	311	335
2	15	139	176
2	16	113	103
3	1	553	-577
3	2	174	-175
3	4	286	-286
3	5	263	276
3	6	87	74
3	7	277	265
3	8	104	97
3	13	118	152
4	1	232	221
4	2	106	106
4	3	289	-289
4	4	220	-228
4	5	299	299
4	6	136	-147
4	7	264	-259
4	8	190	-189
4	10	103	91
4	11	183	171
4	12	281	276
4	13	212	-219

Table S3. Continued

4	15	158	167
5	1	345	-333
5	2	141	146
5	4	171	-163
5	5	228	230
5	6	346	-346
5	7	170	163
5	8	227	-238
5	10	166	162
5	12	307	307
6	1	449	454
6	2	214	-211
6	3	248	-251
6	5	150	139
6	6	217	-200
6	7	248	-261
6	11	145	147
6	13	241	-245
6	14	106	118
7	1	117	82
7	3	214	-214
7	4	166	-164
7	5	213	-205
7	6	220	-215
7	8	109	-133
7	9	283	285
7	10	169	149
7	11	162	162
7	12	193	205
7	13	125	-109
8	1	169	173
8	2	280	-289
8	4	121	117
8	5	162	155
8	6	104	-96
8	7	205	-183
8	8	123	126
8	9	143	-151
8	12	186	-188
9	2	391	-396
9	3	101	-101
9	4	357	-357
10	2	105	-116
10	3	140	124
10	4	233	238
10	6	208	-214
10	7	104	-103
10	9	187	-186
10	11	106	-98
10	12	123	-133
11	1	124	-117
11	2	205	-210
11	3	87	76
11	4	190	-191
11	5	168	172
11	6	94	-98
11	9	155	-153
12	1	75	86
12	3	141	137
12	4	194	201
12	5	172	-163
12	6	136	-136
13	2	76	57
13	6	203	-214
14	1	80	79
14	3	133	141
14	5	187	-186
	H =	6	
K	L	Fo	Fc
0	0	193	200
0	2	344	-366
0	6	338	341
0	8	261	-269
0	10	272	291
1	0	389	-424
1	1	212	-221
1	2	99	-112
1	3	158	157
1	4	195	190
1	5	425	450
1	6	172	175
1	7	219	238
1	9	171	181
1	10	163	-156
1	11	389	-397
1	13	318	-293
1	14	123	142
2	1	149	-159
2	2	246	-259
2	3	87	93
2	6	199	198
2	7	230	-245
2	8	112	-94
2	9	169	166
2	10	303	302
3	0	546	-568
3	1	138	151
3	3	578	586
3	4	91	100
3	5	235	238
3	6	186	184
3	7	183	-193
3	8	141	126
3	10	149	-147
3	14	152	130
3	15	124	-140
4	1	321	-317
4	7	203	-198
4	9	244	244
4	10	178	189
4	11	107	-116
4	15	115	123
5	0	147	-129
5	1	166	172
5	3	365	370
5	4	290	-279
5	5	198	198
5	6	135	-144
5	8	478	474
5	10	212	234
5	14	136	-137
6	0	231	-229
6	1	335	-344
6	7	176	-184
6	8	110	114
6	9	246	229
7	0	207	-204
7	1	87	-87
7	2	88	-71
7	3	107	-102
7	4	105	-119
7	5	99	115
7	7	350	359
7	8	395	387
7	10	178	166
7	11	161	-169
7	13	146	-162
8	0	280	-298
8	1	163	-156
8	5	98	-95
8	7	173	-174
8	8	162	153
8	9	102	96
8	10	126	-156
9	0	520	-546
9	2	194	-190
9	3	128	-133
9	4	189	189
9	6	235	228
9	7	187	179
9	11	93	-35
9	12	95	68
10	0	170	-160
10	2	163	156
10	5	100	-91
10	6	116	-112
10	7	84	-61
10	8	175	152
10	10	102	-108
11	0	230	-243
11	1	219	222
11	2	156	-157
11	3	88	94
11	6	125	122
12	2	77	90
12	3	128	-116
12	8	120	116
13	0	101	89
13	2	103	-103
13	4	153	-134
13	5	86	-88
14	3	141	-136
	H =	7	
K	L	Fo	Fc
0	4	236	248
0	12	118	-114
1	2	350	372
1	3	476	487
1	5	131	-125
1	7	110	-136
1	8	167	-179
1	9	397	-412
1	11	393	-401
1	12	206	203
1	13	271	281
1	15	119	101
2	4	134	153
2	5	89	-86
2	7	91	80
2	12	108	-96
3	1	409	422
3	2	433	456
3	3	177	171
3	5	470	-463
3	6	99	110
3	7	153	-162
3	8	166	-175
3	11	129	-131
3	12	197	197
3	14	157	-156
4	3	141	162
4	5	117	-127
4	7	88	95
5	1	358	377
5	4	179	-181
5	5	219	-224
5	6	551	549
5	7	172	-180
5	8	172	159
5	10	255	-246
5	12	97	-98
5	14	212	-228
6	1	95	-95
6	2	101	94
6	3	98	106
6	5	95	-84
6	6	110	116
6	7	92	86
7	2	165	165
7	5	349	331
7	6	410	402
7	7	146	-161
7	9	291	-289
7	10	184	-183
7	12	101	-129
8	1	78	-83
8	2	79	80
9	2	406	411
9	3	113	-123
9	4	258	249
9	5	268	264
9	7	95	-92
9	8	106	-95
9	9	119	-117
10	3	77	-38
10	4	87	-76
11	1	174	180
11	2	160	163
11	3	194	-196
11	4	231	228
11	9	116	126
12	3	84	-65
12	4	75	-62
13	2	131	-121
13	3	76	-95
13	4	165	158
	H =	8	
K	L	Fo	Fc
0	0	111	-116
1	0	365	403
1	1	295	317
1	3	190	-199
1	4	189	-198
1	5	343	-372
1	6	94	-89
1	7	120	-138
1	9	220	-234
1	10	125	168
1	11	392	402
1	13	218	232
1	14	130	-130
2	0	86	94
2	14	93	-35
3	0	523	531
3	1	93	-106
3	3	476	-499
3	4	116	-114
3	5	238	-235
3	7	218	215
3	8	208	-217
3	9	83	-55
3	10	217	206
3	14	95	-98
4	2	68	41
5	0	220	231
5	1	186	-184
5	2	113	-88
5	3	319	-318
5	4	246	242
5	5	162	-168
5	6	161	162
5	8	467	-464
7	0	302	300
7	1	74	-68
7	3	164	148
7	4	163	168
7	5	126	-122
7	7	342	-350
7	8	370	-375
7	11	109	110
8	3	75	33
9	0	471	464
9	1	121	-126
9	2	166	158
9	3	132	136
9	4	125	-132
9	6	193	-195

Table S3. Continued

K	L	Fo	Fc
9	7	223	-225
9	8	97	-104
9	9	131	138
11	0	172	174
11	1	217	-211
11	2	177	170
11	6	151	-146
13	0	90	-114
13	2	135	143
H = 9			
K	L	Fo	Fc
0	4	263	278
0	6	182	-194
0	12	90	-92
1	1	85	-76
1	2	229	-233
1	3	337	-361
1	4	89	-86
1	7	96	100
1	8	106	113
1	9	313	337
1	11	224	233
1	13	177	-193
2	4	192	195
2	5	194	-199
2	12	120	-125
3	1	286	-302
3	2	349	-357
3	3	87	-92
3	5	349	353
3	6	98	-108
3	7	132	124
3	8	112	109
3	11	110	96
3	12	104	-101
4	1	101	-104
4	2	105	-116
4	3	150	143
4	5	117	-122
4	8	82	86
4	11	93	-89
4	13	92	86
5	1	267	-268
5	3	128	136
5	6	372	-373
5	7	103	107
5	8	110	-108
5	10	147	155
5	12	111	113
6	1	169	-164
6	3	136	138
6	5	91	-55
6	7	96	93
6	11	109	-97
7	2	107	-101
7	5	241	-240
7	6	297	-293
7	7	85	88
7	9	194	200
7	10	110	128
8	2	141	141
8	5	111	-102
9	2	275	-269
9	4	217	-212
9	5	174	-167
9	7	93	82
9	8	95	93
9	9	110	89
10	4	124	-129
11	1	123	-115
11	2	112	-113
11	3	133	128
11	4	192	-191
H = 10			
K	L	Fo	Fc
0	2	270	287
0	4	168	-166
0	6	252	-264
0	8	149	149
0	10	103	-70
1	0	191	-192
1	4	141	154
1	5	236	232
1	6	80	90
1	7	198	204
1	10	120	-102
1	11	212	-235
2	0	90	-103
2	2	180	178
2	3	153	-163
2	6	118	-126
2	7	230	237
2	8	93	82
2	10	135	-153
3	0	266	-269
3	1	151	142
3	2	75	-64
3	3	318	325
3	4	117	103
3	5	152	148
3	6	103	96
4	0	134	-130
4	1	219	220
4	4	131	128
4	7	148	144
4	9	180	-181
4	10	155	-164
5	1	116	117
5	3	222	218
5	4	155	-157
5	8	184	190
5	10	156	151
6	0	153	146
6	1	291	283
6	8	106	-85
6	9	180	-168
7	2	97	-81
7	3	98	-74
7	4	83	-86
7	5	86	95
7	7	174	171
7	8	174	170
7	10	116	118
8	0	231	214
8	1	97	98
8	2	80	-81
8	7	120	117
8	9	78	-68
9	0	257	-234
9	2	160	-149
9	4	105	102
9	6	128	138
9	7	107	101
9	8	79	65
10	0	116	108
10	2	86	-100
10	5	73	60
10	6	111	102
11	0	145	-136
11	1	77	64
11	2	134	-126
H = 11			
K	L	Fo	Fc
0	2	84	-98
0	4	327	-333
0	6	184	186
1	1	103	97
1	2	112	109
1	4	99	101
1	5	109	122
1	6	88	-71
1	7	111	-134
1	9	225	-235
2	4	230	-238
2	5	232	244
2	9	137	-120
3	1	254	248
3	2	108	104
3	4	167	161
3	5	99	-100
3	7	133	-119
4	1	140	143
4	2	102	103
4	3	122	-129
4	5	102	98
4	6	129	-120
4	7	142	-130
4	8	132	-130
5	1	166	165
5	2	81	-71
5	4	113	118
5	5	105	-80
5	8	87	90
6	1	232	214
6	2	101	-86
6	3	144	-136
6	6	81	-58
6	7	128	-130
7	3	97	84
7	4	127	142
7	6	79	82
8	1	80	74
8	2	183	-180
8	5	104	89
8	7	77	-77
9	2	170	145
9	3	73	80
9	4	162	150
10	3	98	84
H = 12			
K	L	Fo	Fc
0	0	190	-205
0	2	182	-186
0	4	162	150
0	6	202	194
0	8	86	-65
1	1	128	-139
1	2	92	74
1	5	106	-93
1	7	188	-200
1	8	84	50
1	9	103	108
2	2	125	-137
2	3	120	122
2	6	79	59
2	7	174	-173
3	1	152	-155
3	2	135	132
3	3	126	-125
3	5	84	-73
3	6	101	-104
3	7	75	-62
3	9	93	81
4	1	127	-114
4	2	75	-63
4	4	124	-115
4	5	85	-65
4	8	145	142
4	9	88	81
5	0	132	-144
5	2	130	125
5	3	92	-83
5	6	99	-85
6	0	124	-101
6	1	183	-167
6	3	138	-143
6	6	74	36
7	1	85	82
7	2	129	113
7	5	111	-83
7	6	77	-63
8	0	192	-180
8	4	79	67
8	5	77	-65
9	0	121	117
9	2	116	100
H = 13			
K	L	Fo	Fc
0	2	256	240
0	4	167	177
1	1	103	-110
1	4	75	-82
1	5	113	-120
1	7	144	123
2	1	96	90
2	2	89	84
2	3	87	-83
2	4	90	80
2	5	106	-110
3	1	125	-119
3	4	141	-137
3	6	77	65
3	7	75	67
4	1	83	-77
4	2	85	-77
4	6	165	161
5	2	94	84
5	4	141	-132
6	1	178	-165
6	2	68	58
7	3	92	-90
H = 14			
K	L	Fo	Fc
0	0	315	311
0	2	75	76
1	1	100	90
2	0	167	151
2	1	116	-98
2	3	68	-66
3	1	102	81
3	2	71	-69
4	3	108	92
5	0	82	63

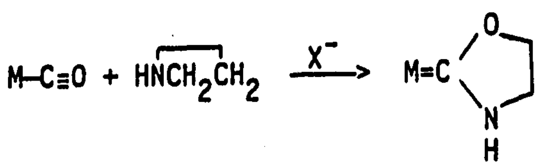
SECTION III. SYNTHESIS AND REACTIONS OF AMINOOXY CARBENE COMPLEXES OF RHENIUM

SUMMARY

The reaction of $Re(CO)_5Br$ and $HNCH_2CH_2$, in the presence of Br^-, gives the aminooxy carbene complex cis-$Re(CO)_4(Br)(=COCH_2CH_2NH)$ (I) at room temperature, but fac-$Re(CO)_3(Br)(=COCH_2CH_2NH)_2$ (II) is obtained in refluxing CH_3CN. Refluxing I with PPh_3 in toluene gives fac-$Re(CO)_3$-$(PPh_3)(Br)(=COCH_2CH_2NH)$ (III). Both I and III are deprotonated by n-BuLi to give the imine complexes, $Re(CO)_4(Br)(-C{=}NCH_2CH_2O)^-Li^+$ and $Re(CO)_3$-$(PPh_3)(Br)(-C{=}NCH_2CH_2O)^-Li^+$, respectively, whose nitrogen atoms are methylated with Me_3O^+ to yield the N-methyl carbenes, $Re(CO)_4(Br)$-$(=COCH_2CH_2NMe)$ (V) and $Re(CO)_3(Br)(PPh_3)(=COCH_2CH_2NMe)$ (IV). The reaction of V with MeLi yields $Re(CO)_4(=COCH_2CH_2NMe)^-Li^+$ which then reacts with MeI to generate the carbene-alkyl compound $Re(CO)_4(CH_3)(=COCH_2CH_2NMe)$ (VI). Upon reaction with potassium hydrotris(1-pyrazolyl)borate, $KHB(pz)_3$, I yields fac-$[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=COCH_2CH_2NH)$ (VII), in which the $HB(pz)_3$ is only bidentate. Under UV photolysis VII loses a CO thereby allowing the third pyrazolyl group to coordinate in $[\eta^3\text{-}HB(pz)_3]Re(CO)_2(=COCH_2CH_2NH)$ (VIII). All of the new compounds are characterized by their IR, ^1H NMR, and ^{13}C NMR spectra.

INTRODUCTION

Our group has reported the synthesis of a number of transition metal complexes containing cyclic dioxy-, aminooxy-, aminothio-, and dithiocarbene ligands [1-4]. The aminooxycarbene complexes were produced by the halide-catalyzed reaction of transition metal carbonyls with aziridine according to eq. 1.



(1)

M: $Fe(CO)_4$, $Re(CO)_4X$ (X = Cl, Br, I), $Mn(CO)_4X$ (X = Cl, Br, I), $CpFe(CO)_2^+$, $CpMn(CO)(NO)^+$, $CpRu(CO)_2^+$, and $CpFe(PPh_3)(CO)^+$.

In the present paper, we report further studies of the aminooxy carbene complex, $Re(CO)_4(Br)(=\overline{COCH_2CH_2N}H)$ (I) in which CO is replaced by phosphine or hydrotris(pyrazolyl)borate ligands, the Br is replaced by CH_3, and the H on the carbene N is replaced by CH_3.

EXPERIMENTAL SECTION

General procedures

All reactions and manipulations were performed using standard Schlenk techniques under prepurified N_2. Unless noted otherwise, reagent grade chemicals were used without further purification. Methylene chloride, hexanes and acetonitrile were distilled from CaH_2 and stored under N_2 over type 4Å molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under N_2.

The starting compounds $Re(CO)_5Br$ [5] and $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$, I, [2] were prepared as reported in the literature. Aziridine [6] ($\overline{CH_2CH_2NH}$) was distilled and stored over KOH before use. Schlenk flasks used in reactions of n-BuLi or CH_3Li were dried in an oven at 120 °C overnight prior to use and then cooled in a dessicator flushed with N_2 [7].

Infrared spectra were recorded on a Perkin-Elmer 681 instrument. ^1H and ^{13}C {^1H} NMR spectra were recorded on a Nicolet 300 MHz spectrometer at room temperature. $Cr(acac)_3$ was added to the solutions to reduce ^{13}C NMR data collection times. Melting points (uncorrected) of the compounds were determined in air on a Thomas Hoover capillary melting-point apparatus. Electron impact mass spectra were obtained using a Finnigan 4000/GC-MS. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

fac-$Re(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2$ (II)

To a mixture of 0.50 g (1.2 mmol) of $Re(CO)_5Br$ and 0.51 g (2.5 mmol) of $BrCH_2CH_2NH_2{\cdot}HBr$ in 20 ml of CH_3CN was added 0.16 ml (3.1 mmol) of aziridine. After being refluxed under N_2 for 5 h, the reaction was complete according to the IR spectrum. The reaction mixture was taken to dryness under vacuum. The yellow residue was dissolved in 20 ml of CH_2Cl_2. After filtering through anhydrous $MgSO_4$, the CH_2Cl_2 solution was concentrated and 30 ml of hexanes was added. It was stored at -20°C overnight to generate yellow microcrystals. Yield: 0.46 g (76%). M.p. 124-127°C. Anal. Found: C, 21.92; H, 1.94; N, 5.48. Calcd for $C_9H_{10}BrN_2O_5Re$: C, 21.95; H, 2.03; N, 5.69. Mass spectrum: m/e (rel. intensity, probable assignment): 491.9 (3.6, M^+); 463.9 (3.56, $(M-CO)^+$); 435.9 (7.24, $(M-2CO)^+$); 408.0 (1.48, $(M-3CO)^+$); 336.9 (14.2, Re(Br)-$(\overline{COCH_2CH_2NH})^+$); 308.9 (16.4, $Re(Br)(CH_2CH_2NH)^+$); 71.0 (100, $COCH_2CH_2NH^+$).

fac-$Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2NH})$ (III)

A mixture of PPh_3 (0.087 g, 0.33 mmol) and I (0.15 g, 0.33 mmol) in 20 ml of toluene was refluxed under N_2 for 15 min. The solvent was removed under vacuum. The colorless residue was extracted with CH_2Cl_2, and hexanes were added until a cloudy solution was observed. The solution was stored overnight at -20°C to give white crystals. Yield: 0.22 g (96%). M.p. 193°C (decomp.). Anal. Found: C, 42.03; H, 3.14; N, 2.08. Calcd. for $C_{24}H_{20}BrNO_4PRe$: C, 42.16; H, 2.93; N, 2.05. Mass spectrum: m/e (rel. intensity, probable assignment): 683.0 (7.9, M^+); 654.8 (17.1,

$(M-CO)^+$); 626.7 (29.0, $(M-2CO)^+$); 598.7 (30.6, $(M-3CO)^+$); 527.6 (5.9, $Re(PPh_3)(Br)^+$); 262 (100, PPh_3).

fac-$Re(CO)_3(PPh_3)(Br)[=\overline{COCH_2CH_2N}(CH_3)]$ (IV)

A slight excess of n-BuLi (0.30 ml of 2.4 M n-BuLi in hexane, 0.72 mmol) was injected into a solution of 0.46 g (0.68 mmol) of $Re(CO)_3(PPh_3)$-$(Br)(=\overline{COCH_2CH_2NH})$, III, in 50 ml of freshly distilled THF at -78°C to generate the deprotonated imine complex, $Re(CO)_3(PPh_3)(Br)(-\overline{C{=}NCH_2CH_2O})^-$ Li^+. At -78°C, 0.15 g (0.72 mmol) of $Me_3O^+PF_6^-$ was added to the yellow solution. After stirring for 5 h at room temperature, the mixture was filtered through anhydrous $MgSO_4$, and then the solvent was removed under vacuum. The yellow residue was chromatographed on a silica gel column (2.5 x 15 cm) using CH_2Cl_2 as the eluent to give a colorless solution. The solvent was removed under vacuum. Colorless crystals of the product were obtained from CH_2Cl_2/hexanes at -20°C. Yield: 0.37 g (78%). M.p. 97-99°C. Anal. Found: C, 42.19; H, 3.14; N, 1.75. Calcd. for $C_{25}H_{22}BrNO_4PRe{\bullet}0.1\ CH_2Cl_2$: C, 42.66; H, 3.12; N, 1.98. Mass spectrum: m/e (rel. intensity, probable assignment): 696.9 (2.0, M^+); 668.9 (6.0, $(M-CO)^+$); 641.0 (8.0, $(M-2CO)^+$); 612.9 (2.0, $(M-3CO)^+$); 434.9 (17, $Re(CO)_3(Br)(=\overline{COCH_2CH_2N}Me)^+$); 406.9 (32, $Re(CO)_2(Br)(=\overline{COCH_2CH_2N}Me)^+$); 262.1 (100, PPh_3).

cis-$Re(CO)_4(Br)[=\overline{COCH_2CH_2N}(CH_3)]$ (V)

One equivalent of n-BuLi (0.30 ml, 2.4 M of n-BuLi in hexanes, 0.72 mmol) was injected into a 50 ml THF solution of 0.32 g (0.72 mmol) of

$Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ at -78°C. Keeping the temperature at -78°C, 0.15 g (0.72 mmol) of $Me_3O^+PF_6^-$ was added. After the solution was allowed to reach room temperature, it was stirred for 2 h. The pale yellow solution was taken to dryness, and the residue was chromatographed on a silica gel column (2.5 x 16 cm). The first band (pale yellow) which was eluted with 1:1 CH_2Cl_2/hexanes gave a minor product which was possibly $Re(CO)_4(CH_3)$-$(=\overline{COCH_2CH_2NH})$. The second band (pale yellow) eluted with 2:1 CH_2Cl_2/hexanes and contained compound **V**. The latter solution was evaporated under vacuum to yield a pale yellow powder, which was recrystallized from CH_2Cl_2/hexanes at -20°C to give pale yellow crystals of $Re(CO)_4(Br)$-$[=\overline{COCH_2CH_2N}(CH_3)]$. Yield: 0.10 g (32%). M.p. 129-132°C. Anal. Found: C, 20.87; H, 1.60; N, 2.99. Calcd. for $C_8H_7BrNO_5Re$: C, 20.73; H, 1.51; N, 3.02. Mass spectrum: m/e (rel. intensity, probable assignment): 462.9 (79.4, M^+); 434.9 (70.3, $(M-CO)^+$); 406.9 (100, $(M-2CO)^+$); 378.9 (14.4, $(M-3CO)^+$); 350.9 (3.71, $(M-4CO)^+$), 323.0 (5.52, $Re(Br)$-$(CH_2CH_2NMe)^+$).

cis-$Re(CO)_4(CH_3)[=\overline{COCH_2CH_2N}(CH_3)]$ (**VI**)

A slight excess of CH_3Li (0.20 ml of 1.4 M CH_3Li in Et_2O, 0.28 mmol) was injected into a 30-ml THF solution of $Re(CO)_4(Br)[=\overline{COCH_2CH_2N}(CH_3)]$ (**V**) (0.13 g, 0.27 mmol) at -78°C, and then excess CH_3I (0.10 ml, 1.6 mmol) was added. After being stirred at room temperature for 5 h, the mixture was taken to dryness under vacuum at 0°C because of the high volatility of the product. The yellow oily residue was chromatographed on a silica gel column (2.5 x 10 cm). The colorless band was eluted with 1:1 CH_2Cl_2/

hexanes, and the solution was evaporated under vacuum at 0°C to generate pure white solid VI. Yield: 0.070 g (64%). M.p. 119-120°C. Anal. Found: C, 27.31; H, 2.80; N, 3.38. Calcd. for $C_9H_{10}NO_5Re$: C, 27.12; H, 2.51; N, 3.52. Mass spectrum: m/e (rel. intensity, probable assignment): 399.0 (22.2, M^+); 384.0 (100, $(M-CH_3)^+$); 356 (73.5, $(M-CH_3-CO)^+$); 328 (51.3, $(M-CH_3-2CO)^+$); 313.0 (52.3, $Re(CO)_2(=\overline{COCH_2CH_2N})^+$); 300.0 (22.9, $(M-CH_3-3CO)^+$); 272.0 (6.11, $(M-CH_3-4CO)^+$).

fac-[η^2-HB(pz)$_3$]Re(CO)$_3$(=$\overline{COCH_2CH_2N}$H) (VII)

A solution of 0.090 g (0.34 mmol) of potassium hydrotris(pyrazolyl)-borate, KHB(pz)$_3$, and 0.15 g (0.34 mmol) of Re(CO)$_4$(Br)(=$\overline{COCH_2CH_2N}$H) (I) in 40 ml of THF was refluxed and stirred under N_2 for 18 h. A colorless solution and white precipitate were obtained. The mixture was filtered through anhydrous $MgSO_4$, and the solvent was removed under vacuum. The white residue was recrystallized from CH_2Cl_2/hexanes at -20°C. Colorless crystals were obtained. Yield: 0.10 g (55%). Anal. Found: C, 32.63; H, 3.00; N, 17.58. Calcd. for $C_{15}H_{15}BN_7O_4$ Re: C, 32.49; H, 2.71; N, 17.69. Mass spectrum: (No parent ion (M^+) peak was observed at 555 (for the most intense peak which contains ^{11}B and ^{187}Re isotopes), but it did show peaks due to its fragments.) m/e (rel. intensity, probable assignment): 527.4 (12.8, $(M-CO)^+$); 499.4 (1.9, $(M-2CO)^+$); 484.3 (26.3, $(M-CH_2CH_2NH)^+$); 400.3 (33.9, $HB(pz)_3Re^+$); 68.0 (100, $C_3H_4N_2^+$).

$[\eta^3\text{-}HB(pz)_3]Re(CO)_2(=\overline{COCH_2CH_2NH})$ (VIII)

A 35 ml THF solution of 0.26 g (0.47 mmol) of $[\eta^2\text{-}HB(pz)_3]Re(CO)_3\text{-}(=\overline{COCH_2CH_2NH})$ was photolyzed in a quartz tube at λ = 254 nm for 18 h when the reaction was complete (IR evidence). A pale brown solution was obtained. The solvent was removed under vacuum and the residue was chromatographed on a silica gel column (2.5 x 10 cm). A pale yellow band containing the product was eluted with 2:1 CH_2Cl_2/hexanes. The solution was taken to dryness. Pale yellow microcrystals were obtained by recrystallization from CH_2Cl_2/hexanes at -20°C. Yield: 0.060 g (23%). M.p. 202°C (decomp.). Anal. Found: C, 31.58; H, 2.83; N, 18.07. Calcd. for $C_{14}H_{15}BN_7O_3Re \cdot 0.06\ CH_2Cl_2$: C, 31.77; H, 2.85; N, 18.45. Mass spectrum: m/e (rel. intensity, probable assignment): 527.1 (100, M^+); 499.1 (5.85, $(M\text{-}CO)^+$); 456.0 (5.11, $HB(pz)_3Re(CO)_2^+$); 443.1 (26.6, $(M\text{-}3CO)^+$); 415.1 (31.8, $HB(pz)_3Re(NH)^+$); 400.1 (36.1, $HB(pz)_3Re^+$).

RESULTS AND DISCUSSION

The aminooxycarbene complex cis-$Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) was prepared previously [2] by reaction of $Re(CO)_5Br$ with aziridine and $BrCH_2CH_2NH_3^+Br^-$ in CH_3CN at room temperature for 15 min (eq. 1). We now find that refluxing this mixture for 5 h with additional aziridine yields (76%) the bis(carbene) complex, II, eq. 2. It seems that both aziridine

$$Re(CO)_5Br + 2\ HN\triangleleft \xrightarrow[CH_3CN]{BrCH_2CH_2NH_2\cdot HBr} fac\text{-}Re(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2 \qquad (2)$$

II

and $BrCH_2CH_2NH_3^+Br^-$ are required in order to obtain maximum yields of I or II from the reaction. If the reaction is performed by generating aziridine in situ from $BrCH_2CH_2NH_3^+Br^-$ and NaH (2 eqt.), some $Re(CO)_5Br$ remains unreacted even after stirring for 4 days in CH_3CN at room temperature. When this reaction is carried out in refluxing CH_3CN for 30 min, all of the $Re(CO)_5Br$ reacts to give a mixture of **I** and **II**. IR spectra taken during the reaction in eq. 2 show the presence of $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) as an intermediate which converts to the biscarbene compound, II, by further reaction with $H\overline{NCH_2CH_2}$. The 3 nearly equally-intense ν(CO) absorptions in the IR spectrum of II (Table 1) indicate a facial geometry for II. A similar biscarbene complex, $Mn(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2$, has been synthesized from $Mn(CO)_5Br$ and two equivalents of $CNCH_2CH_2OH$ in Et_2O at room temperature for 1 d [8]. The IR spectrum of

Table 1. IR data for the complexes in CH_2Cl_2 solvent

Complex	IR, ν(CO), cm^{-1}
cis-Re(CO)$_4$(Br)(=$\overline{COCH_2CH_2NH}$), I	2115 m, 2009 vs, 1941 s
fac-Re(CO)$_3$(Br)(=$\overline{COCH_2CH_2NH}$)$_2$, II	2040 vs, 1939 s, 1904 s
fac-Re(CO)$_3$(PPh$_3$)(Br)(=$\overline{COCH_2CH_2NH}$), III	2039 vs, 1946 s, 1905 s
fac-Re(CO)$_3$(PPh$_3$)(Br)[=$\overline{COCH_2CH_2N}$(CH$_3$)], IV	2038 vs, 1943 s, 1904 s
cis-Re(CO)$_4$(Br)[=$\overline{COCH_2CH_2N}$(CH$_3$)], V	2113 m, 2015 s, 1999 s, 1940 s
cis-Re(CO)$_4$(CH$_3$)[=$\overline{COCH_2CH_2N}$(CH$_3$)], VI	2079 m, 1975 s, 1964 s, 1915 s
fac-[η^2-HB(pz)$_3$]Re(CO)$_3$(=$\overline{COCH_2CH_2NH}$), VII	2033 s, 1930 s, 1894 s
[η^3-HB(pz)$_3$]Re(CO)$_2$(=$\overline{COCH_2CH_2NH}$), VIII	1923 s, 1829 s

$Mn(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2$ (ν(CO)(KBr) = 2018 vs, 1932 vs, 1905 sh, 1898 vs) is similar to that of compound II (Table 1).

The reaction (eq. 3) of I with an equimolar amount of PPh_3 in

$$Re(CO)_4(Br)(=\overline{COCH_2CH_2NH}) + PPh_3 \xrightarrow{\text{toluene}} \quad (3)$$

I

$$fac\text{-}Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2NH}) + CO \quad (3)$$

III

refluxing toluene gives fac-$Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2NH})$ (III) in 96% yield within 15 min. As for II, the 3 ν(CO) bands in the IR spectrum (Table 1) of III indicate that it also has a facial structure; the spectrum is also very similar to that of the previously reported fac-$Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2O})$ (2038 s, 1958 s, 1906 s cm^{-1}) [9]. The similarity of the ν(CO) frequencies for II and III suggest that the $=\overline{COCH_2CH_2NH}$ and PPh_3 ligands have comparable electronic properties, as has been noted previously [10]. The asymmetric Re center in III causes the protons in the carbene ligand to be diastereotopic and give an ABCD pattern in the ^1H NMR spectrum; thus, four multiplets are observed at 2.88, 3.40, 3.94, 4.44 ppm (Table 2). In the ^{13}C NMR spectrum of III (Table 3) the doublet ($^2J_{PC}$ = 60.1 Hz) at 189.19 ppm is assigned to the CO trans to PPh_3, and the other two doublets at 194.59 and 189.31 ppm with coupling constants of 8.60 and 7.39 Hz are assigned to the CO ligands cis to the PPh_3. In other Re(I) complexes, $Re(CO)_4(dppe)^+$,

Table 2. ^{1}H NMR data for the complexes in $CDCl_3$ solvent at room temperature[a]

Complex	-NCH_2-	-OCH_2-	-NH-	Others
I	3.80 (t)[b]	4.77 (t)[b]	9.05 (br)	
II	3.77 (m)	4.66 (m)	8.93 (br)	
III	3.40 (m)	4.44 (m)	8.63 (br)	7.66 (m), 7.39 (m) (PPh_3)
	2.88 (m)	3.94 (m)		
IV	3.34 (m)	4.18 (m)		3.69 (s) (NCH_3)
	3.18 (m)	3.52 (m)		7.60 (m), 7.39 (m) (PPh_3)
V	3.81 (t)[c]	4.65 (t)[c]		3.58 (s) (NCH_3)
VI	3.70 (t)[d]	4.56 (t)[d]		-0.46 (s) ($ReCH_3$)
				3.39 (s) (NCH_3)
VII[i]	3.68 (m)	4.57 (m)	9.26 (br)	7.36 (m) ($H_3$and H_5 of pz)
				6.18 (m) (H_4 of pz)
VIII[i]	3.72 (t)[e]	4.50 (t)[e]	8.16 (br)	7.80 (d, 1H)[f], 7.67 (d, 2H)[f] (H3 of pz); 6.19 (t, 3H)[g] (H4 of pz); 7.77 (d, 2H)[h], 7.74 (d, 1H)[h] (H5 of pz)

[a]Chemical shifts in δ (relative to $Si(CH_3)_4$) and coupling constants in Hz.

[b] J = 9.77 Hz.

[c] J = 9.89 Hz.

[d] J = 9.74 Hz.

[e] J = 9.06 Hz.

[f] J = 1.47 Hz.

[g] J = 2.06 Hz.

[h] J = 2.22 Hz.

[i] acetone-d_6 solvent.

Table 3. ^{13}C NMR data[a] for the complexes in $CDCl_3$ solvent at room temperature[a]

Complex	Carbene C	Carbonyl	OCH_2	NCH_2	Others
I[b]	208.19	188.60 186.09 185.13	73.24	45.59	
II[c]	217.18	193.12 192.72 188.81	71.94	44.36	
III[c]	216.88 (d)[e]	194.59 (d)[f] 189.19 (d)[g] 189.31 (d)[h]	71.46	43.48	133.36 (d) 132.72, 132.13 129.82 127.74 (d) (PPh_3)
IV[d]	213.02 (d)[i]	194.65 (d)[j] 191.80[k] (d) 191.13[l] (d)	70.74	52.33	37.94 (NCH_3); 134.81 (d) 134.46, 134.26, 130.85 128.82 (d) (PPh_3)

[a]Chemical shifts in δ (relative to $Si(CH_3)_4$) and coupling constants in Hz.

[b]In CD_3CN solvent.

[c]In CD_2Cl_2 solvent.

[d]In d_6-acetone solvent.

[e]J_{PC} = 8.76 Hz.

[f]J_{PC} = 8.60 Hz. CO cis to PPh_3.

[g]J_{PC} = 60.1 Hz. CO trans to PPh_3.

[h]J_{PC} = 7.39 Hz. CO cis to PPh_3.

[i]J_{PC} = 9.90 Hz. cis to PPh_3.

[j]J_{PC} = 6.75 Hz. CO cis to PPh_3.

[k]J_{PC} = 235 Hz. CO trans to PPh_3.

[l]J_{PC} = 7.40 Hz. CO cis to PPh_3.

Table 3. Continued

Complex	Carbene C	Carbonyl	OCH_2	NCH_2	Others
V	208.56	185.51 184.82[m] 183.24	70.30	51.32	37.49 (NCH_3)
VI	213.15	191.18[m] 190.19 187.98	69.95	50.66	37.02 (NCH_3) -32.73 ($ReCH_3$)
VII[d]	219.40 218.90	196.52 196.26 194.45 191.84	72.05 71.51	54.86 45.14	146.90, 146.02, 144.93, 142.39, 141.67 (C_3 of pz); 137.93, 136.12, 134.66, 132.03 (C_5 of pz); 107.64, 106.70, 106.51, 105.43, 105.33, 104.88 (C_4 of pz)
VIII[d]	209.69	not observed	70.63	45.59	146.39, 144.74 (C_3 of pz); 135.42 (C_5 of pz); 106.57, 106.36 (C_4 of pz)

[m]Two CO groups trans to each other.

$Re(CO)_3(dppe)[=C(OEt)(SiPh_3)]^+$ and $Re(CO)_3(dppe)(COSiPh_3)$, ^{13}CO coupling constants to cis and trans phosphines are 6-9 and 40-60 Hz, respectively [11].

The neutral imine complex, $CpFe(CO)_2(-C{=}NCH_2CH_2O)$, can be produced by deprotonation of the aminooxycarbene, $CpFe(CO)_2(=COCH_2CH_2NH)^+BF_4^-$, in CH_2Cl_2 by K_2CO_3 or NaH [10]; this imine complex reacts with electrophiles (E^+) [12] (e.g., $Me_3O^+PF_6^-$ or allyl bromide) yielding the N-alkyl carbene compounds (eq. 4). Similarly, the diaminocarbene

$$[M{=}COCH_2CH_2NH]^+ \xrightarrow[-HB^+]{:B} M{-}C{=}NCH_2CH_2O \xrightarrow{E^+} [M{=}COCH_2CH_2NE]^+ \qquad (4)$$

trans-$\{(PPh_3)_2Pt[CN(p\text{-}MeC_6H_4)CH_2CH_2N(H)]Br\}BF_4$ reacts with n-BuLi at -8°C to give the intermediate imino complex trans-$\{(PPh_3)_2Pt$-$[CN(p\text{-}MeC_6H_4)CH_2CH_2N]Br\}$ which rapidly reacts with allyl bromide or propargyl bromide to afford the corresponding N-substituted products [13]. Attempts to deprotonate the carbene nitrogen atoms in $Re(CO)_4(Br)$-$(=COCH_2CH_2NH)$ (I) with the bases, NaH, $LiAlH_4$, $NaN(SiMe_3)_2$ and $Re(CO)_3(PPh_3)(Br)(=COCH_2CH_2NH)$ (III) with NaH were unsuccessful. However, I is deprotonated by n-BuLi, PhLi or NaNp and III is deprotonated by n-BuLi to produce the imine complexes, $Re(CO)_4(Br)(-C{=}NCH_2CH_2O)^-Li^+$ and $Re(CO)_3(PPh_3)(Br)(-C{=}NCH_2CH_2O)^-Li^+$ (eq. 5). These anionic imine compounds have IR spectra with $\nu(CO)$ relative intensities similar to their aminooxycarbene precursors (I and III), but the $\nu(CO)$ positions are about 15-20 cm^{-1} lower.

$$Re(CO)_3(L)(Br)(=\overline{COCH_2CH_2NH}) \xrightarrow[-n\text{-}BuH]{n\text{-}BuLi} Re(CO)_3(L)(Br)(=\overline{COCH_2CH_2N})^- \quad (5)$$

$$\xrightarrow{Me_3O^+} fac\text{-}Re(CO)_3(L)(Br)[=\overline{COCH_2CH_2N}(CH_3)]$$

IV: L = PPh_3

V: L = CO

The N atom of the anionic imine complexes reacts with $Me_3O^+BF_4^-$ to give the N-methyl carbenes, $Re(CO)_4(Br)(=\overline{COCH_2CH_2N}Me)$ (**V**) and $Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2N}Me)$ (**IV**) (eq. 5) in 64% and 78% isolated yields. The $-CH_2CH_2-$ region of the ^1H NMR spectrum of $Re(CO)_3(PPh_3)(Br)$-$(=\overline{COCH_2CH_2N}Me)$ (**IV**) shows a pattern similar to that in III (4 sets of multiplets at 3.18, 3.34, 3.52 and 4.18 ppm) as expected for an ABCD system. The 3 ν(CO) bands of **IV** and 4 ν(CO) bands of **V** in their IR spectra (Table 1) suggest that they have facial and cis structures, respectively, as for the related complexes I and III. The ^{13}C NMR spectrum of V has 3 carbonyl peaks, 185.51, 184.82 and 183.24 ppm, with approximate relative intensities of 1:2:1.

The reaction of $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ with n-BuLi gives not only the deprotonated anionic imine compound $Re(CO)_4(Br)(-\overline{C{=}NCH_2CH_2O})^-Li^+$, but apparently also the reduced $Re(CO)_4(=COCH_2CH_2NH)^-Li^+$ product, as suggested by the generation of a small amount (10%) of a byproduct, $Re(CO)_4(CH_3)$-$(=\overline{COCH_2CH_2NH})$ which was identified by its IR and ^1H NMR spectra (ν(CO), in CH_2Cl_2: 2068 m, 1954 vs, 1919 s cm^{-1}; δ, in $CDCl_3$: 0.06 (s, 3H, Re-Me);

3.70 (t, 2H, J = 9.2 Hz, $-NCH_2-$); 4.58 (t, 2H, J = 9.5 Hz, $-OCH_2-$) 7.44 (br, 1H, -NH-) ppm).

The reaction of $Re(CO)_4(Br)(=\overline{COCH_2CH_2N}Me)$ (**V**) and methyl lithium in THF at -78°C generates $Re(CO)_4(=\overline{COCH_2CH_2N}Me)^-Li^+$ whose IR spectrum (ν(CO): 2002 s, 1910 s, 1872 vs cm^{-1}) is similar to that reported previously for $Mn(CO)_4(PPh_3)^-Na^+$ [14] at 1941 s, 1846 ms, 1815 vs cm^{-1}. This anionic intermediate reacts with MeI to give $Re(CO)_4(CH_3)$-$(=\overline{COCH_2CH_2N}Me)$ (**VI**) in 64% yield (eq. 6). The presence of 4 ν(CO) bands

$$Re(CO)_4(Br)[=\overline{COCH_2CH_2N}(CH_3)] \xrightarrow{CH_3Li} Re(CO)_4[=\overline{COCH_2CH_2N}(CH_3)]^-Li^+$$

V

$$\xrightarrow{MeI} cis\text{-}Re(CO)_4(CH_3)[=\overline{COCH_2CH_2N}(CH_3)] \qquad (6)$$

VI

in the IR spectrum (Table 1) of **VI** indicates that it has a cis structure.

Recently there has been considerable theoretical [15] and synthetic [16] interest in carbene-alkyl complexes as models for possible species present on catalyst surfaces in the Fischer-Tropsch reaction. There are, however, only two known examples of carbene-alkyl complexes also containing CO ligands, $Ir(Cl)(CO)(PPhMe_2)_2(Me)(=C(OMe)Me)^+PF_6^-$ [17] and the dinuclear $Me(CO)_3Re(\mu\text{-}PPh_2)_2W(CO)_3(=C(OEt)Me)$ [18]. Thus, we were interested in exploring the possibility of CH_3 migration onto the carbene or CO ligand in complex **VI**. Unfortunately, refluxing PPh_3 or PMe_3 with **VI** in benzene generates very low yields of only phosphine-substituted products, possibly fac-$Re(CO)_3(PR_3)(CH_3)(=\overline{COCH_2CH_2NMe})$, although efforts to characterize it were unsuccessful. Also, photolysis of PPh_3 or PMe_3 with VI in THF gives primarily decomposition products. The lack of CH_3 migration in this system may reflect the unreactivity of $MeRe(CO)_5$ which does not give the acyl complex $MeCORe(CO)_5$ even under 320 atm of CO at 140°C; further heating to 200° leads only to $Re_2(CO)_{10}$ [19].

The reaction of $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) with $Na(C_5H_5)$ in refluxing THF gives only the deprotonated product $Re(CO)_4(Br)(-\overline{C{=}NCH_2CH_2O})^-Na^+$, as determined by the IR spectrum of the solution. When I reacts with $Li^+(C_5Me_5)^-$, no stable complex could be isolated. However, complex I reacts with the hydrotris(pyrazolyl)borate, $HB(pz)_3^-$, ligand in refluxing THF for 18 h to yield $[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2NH})$ (VII) (eq. 7). The IR spectrum of VII exhibits three strong bands of

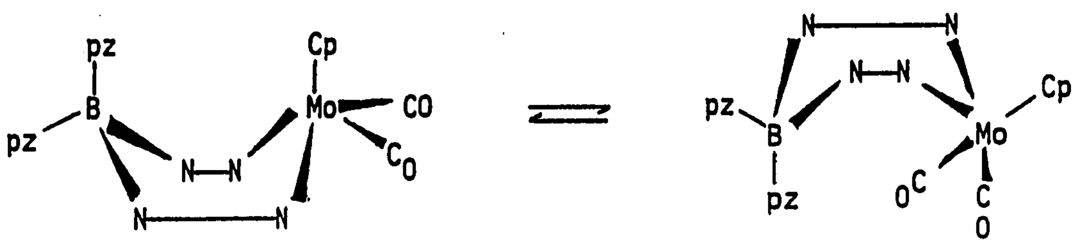
$$K[HB(pz)_3] + \underset{\textbf{I}}{Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})}$$

$$\xrightarrow{THF} \underset{\textbf{VII}}{[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2NH})} + KBr + CO \qquad (7)$$

approximately equal intensity at 2033, 1930 and 1894 cm^{-1}, which is consistent with a facial arrangement of the three CO ligands. In order to accommodate the 18 electron rule, the presence of three carbonyls and one carbene ligand requires that only two of the three pyrazolyl groups in

$HB(pz)_3^-$ coordinate to the metal which leaves the third one uncoordinated. Although the IR spectrum in the ν(CO) region of **VII** is consistent with the presence of only one fac isomer, the four CO and two carbene C resonances in the ^{13}C NMR spectrum suggest the presence of two isomers. The structures of these isomers is not entirely clear. Previously, two isomers were observed [20] in the NMR spectra of $[\eta^2\text{-}B(pz)_4](\eta^5\text{-}Cp)(CO)_2Mo$ and attributed to the two structures in Figure 1, resulting from the shallow boat configuration of the chelate ring. Similar structures were proposed [21] for the two observed isomers of $CpRu[\eta^2\text{-}HB(3,5\text{-}Me_2pz)_3](CO)$. It is possible that **VII** exists as similar isomers; however, the two isomers resulting from interchanging the non-coordinated H and pz groups on the B cannot be excluded. The ^1H NMR spectrum of **VII** at room temperature consists of multiplets at 3.68 and 4.57 ppm and a broad band at 9.26 ppm which can be assigned to the NCH_2CH_2O and NH protons of the aminooxycarbene group and a complex group of resonances between 6.0 and 8.0 ppm which are due to the protons on the pyrazolyl rings. The two multiplets for the OCH_2 and NCH_2 protons suggest that more than one isomer is present. The complicated pattern for H3, H4 and H5 in the pyrazolyl ligand also suggests the presence of isomers.

Refluxing the bidentate derivative $[\eta^2\text{-}HB(pz)_3]Re(CO)_3(\overline{=COCH_2CH_2NH})$ in THF (2 days, no reaction) or dimethylformamide (1 day, decomposition) does not force the third pyrazolyl group to coordinate to the metal; however, when a THF solution of $[\eta^2\text{-}HB(pz)_3]Re(CO)_3(\overline{=COCH_2CH_2NH})$ is photolyzed with UV light, the tridentate $[\eta^3\text{-}HB(pz)_3]Re(CO)_2(\overline{=COCH_2CH_2NH})$ (**VIII**) is obtained (eq. 8). The IR and ^1H NMR spectra of **VIII** are



A

B

Fig. 1. Possible isomers of $[\eta^2\text{-}B(pz)_4](\eta^5\text{-}C_5H_5)(CO)_2Mo$

consistent with the presence of a tridentate pyrazolylborate ligand. The presence of 2 ν(CO) bands of approximately equal intensity at 1923 and 1829 cm^{-1} indicates that the two CO ligands are cis to each other [22]. The ^{1}H NMR spectrum (Table 2) exhibits two sets of pyrazolyl resonances

$$[\eta^2\text{-HB(pz)}_3]\text{Re(CO)}_3(=\overline{\text{COCH}_2\text{CH}_2\text{N}}\text{H})$$

VII

$$\xrightarrow[\text{THF}]{h\nu} [\eta^3\text{-HB(pz)}_3]\text{Re(CO)}_2(=\overline{\text{COCH}_2\text{CH}_2\text{N}}\text{H}) + \text{CO} \quad (8)$$

VIII

with an intensity ratio of 2:1. Assignments of the H3, H4, and H5 protons were made following those of Trofimenko [23] and are given in Table 2. Attempts to convert **VIII** back to **VII** by reacting THF solutions of **VIII** with up to 35 atm of CO at 75°C yielded no evidence for the reformation of **VII** (the only metal carbonyl compound is starting material **VIII**).

CONCLUSION

The carbene ligand in <u>cis</u>-$Re(CO)_4(Br)(=\overline{COCH_2CH_2N}H)$ (I) is sufficiently stable that a variety of reactions can be performed on I without affecting the carbene ligand. The NH group may be deprotonated and the resulting imine methylated (eq. 5). The CO ligands may be substituted by PPh_3 (eq. 3) or $HB(pz)_3^-$ (eq. 7 and 8), and the Br ligand may be replaced in the N-methyl complex (V) by a methyl.

Acknowledgment

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

1. Singh, M. M.; Angelici, R. J. Angew. Chem. Int. Ed. Engl. 1983, 22 163; Angew. Chem. Suppl. 1983, 22, 184.
2. Singh, M. M.; Angelici, R. J. Inorg. Chem. 1984, 23, 2699.
3. Singh, M. M.; Angelici, R. J. Inorg. Chem. 1984, 23, 2691.
4. Singh, M. M.; Angelici, R. J. Inorg. Chim. Acta 1985, 100, 57.
5. Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. Inorg. Chem. 1962, 1, 933; Schmidt, S. P.; Trogler, W. C.; Basolo, F. Inorg. Synth. 1985, 23, 41.
6. Wystrach, V. P.; Kaiser, D. W.; Schaefer, F. C. J. Am. Chem. Soc. 1955, 77, 5915; J. Am. Chem. Soc. 1956, 78, 1263.
7. Shriver, D. F.; Drezdzon, M. A. "The Manipulation of Air-Sensitive Compounds", Wiley-Interscience: New York, 1986, p. 11.
8. Fehlhammer, W. P.; Plaia, U. Z. Naturforsch. 1986, 41B, 1005.
9. Miessler, G. L.; Kim, S.; Jacobson, R. A.; Angelici, R. J. Inorg. Chem. 1987, 26, 1690.
10. Motschi, H.; Angelici, R. J. Organometallics 1982, 1, 343.
11. Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981; pp. 165-166.
12. Johnson, L. K.; Angelici, R. J. Inorg. Chem. 1987, 26, 973.
13. Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. Inorg. Chem., 1988, 27, 93.
14. Faltynek, R. A.; Wrighton, M. S. J. Am. Chem. Soc. 1978, 100, 2701.
15. Ziegler, T.; Versluis, L.; Tschinke, V. J. Am. Chem. Soc. 1986, 108, 612.
16. For example: (a) Werner, H.; Kletzin, H.; Höhn, A.; Paul, W.; Knaup, W. J. Organomet. Chem. 1986, 306, 227. (b) Thorn, D. L. Organometallics 1986, 5, 1897.
17. Clark, H. C.; Reimer, K. J. Inorg. Chem. 1975, 14, 2133.
18. Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L. Organometallics 1985, 4, 1418.

19. King, R. B.; King, Jr., A. D.; Iqhal, M. Z.; Frazier, C. C. J. Am. Chem. Soc. 1978, 100, 1687.

20. Calderson, J. L.; Cotton, F. A.; Shaver, A. J. Organomet. Chem. 1972, 37, 127.

21. McNair, A. M.; Boyd, D. C.; Mann, K. R. Organometallics 1986, 5, 303.

22. Brisdon, B. J. J. Organomet. Chem. 1977, 125, 225; Reimann, R. H.; Singleton, E. J. Chem. Soc., Dalton Trans. 1973, 2658.

23. Trofimenko, S. Prog. Inorg. Chem. 1986, 34, 115.

SECTION IV. PLATINUM(O) COMPLEXES AS CATALYSTS OF METAL CARBONYL SUBSTITUTION REACTIONS

ABSTRACT

The reaction between metal carbonyls ($Fe(CO)_5$, $W(CO)_6$, $CpFe(CO)_2I$, $Re(CO)_5(CH_3)$, $Re_2(CO)_{10}$, and $Os_3(CO)_{12}$) and PPh_3 in refluxing benzene is catalyzed by $Pt(PPh_3)_4$ and yields the mono-substituted compounds as the only products (72-98%). The substitution of $Fe(CO)_5$ by PPh_3 and PMe_2Ph and $CpFe(CO)_2I$ by PPh_3 and $P(OMe)_3$ are also catalyzed by $Pt(dba)_2$, dba = dibenzylideneacetone, suggesting that $Pt(dba)_2$ may be of general utility as a catalyst for substitution reactions of metal carbonyls with monodentate phosphines. Evidence is presented which indicates that the reactions proceed by electron transfer catalysis (ETC) involving radical intermediates.

INTRODUCTION

Phosphine-substituted metal carbonyls have often been prepared by methods involving thermal or photochemical replacement of a CO ligand, despite several commonly-observed problems: low yields, mixtures of mono- to multi-substituted products and long reaction times [1]. More recently, several new procedures [2] have been developed to promote CO substitution by other ligands under mild conditions. Among them is Me_3NO [3], which oxidatively decarbonylates metal carbonyls leading to a coordinatively unsaturated intermediate. Sodium benzophenone ketyl (BPK) [4,5] has been shown to catalyze CO substitution. Also several transition metal complexes induce catalytic CO displacement in metal carbonyls. These include $[CpFe(CO)_2]_2$ [6], $[CpMo(CO)_3]_2$ [7], $CoCl_2$ [8], PdO [9], and $Fe_2(CO)_6(SMe)_2$ [10]. In most of these reactions, there is evidence for or it has been suggested that electron transfer catalysis (ETC) is involved. We report here that the Pt(0) complexes, $Pt(PPh_3)_4$ and $Pt(dibenzylideneacetone)_2$, $(Pt(dba)_2)$, also catalyze the phosphine substitution of CO in mono-, di-, and trinuclear metal carbonyl complexes. These two catalysts offer a convenient, high yield route to monosubstituted $M_x(CO)_{y-1}L$ complexes where L is a monodentate P-donor ligand.

EXPERIMENTAL SECTION

General

All reactions were performed under prepurified N_2. Unless noted otherwise, reagent grade chemicals were used without further purification. Methylene chloride and hexanes were distilled from CaH_2 and stored under N_2 over type 4Å molecular sieves. Benzene was distilled from sodium benzophenone under N_2.

The starting compounds, $W(CO)_6$, $Fe(CO)_5$, $CpMn(CO)_3$, $Re_2(CO)_{10}$, and $Ph_2PCH_2CH_2PPh_2$ (dppe) were purchased from Pressure Chemical Co. Other starting compounds, $CpFe(CO)_2I$ [11], $Re(CO)_5(CH_3)$ [12], $Pt(PPh_3)_4$ [13], and $Pt(dba)_2$ [14], were prepared as reported in the literature. The compound $Os_3(CO)_{12}$ was prepared from OsO_4 by a modification of a literature procedure [15] which was carried out in a 300 mL stainless steel pressure autoclave (Parr. model no. 4761).

Infrared spectra were recorded on a Perkin-Elmer 681 instrument. ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer. Electron impact mass spectra were obtained using a Finnigan 4000 GC-MS.

Reaction of metal carbonyls with PPh_3 in the presence of $Pt(PPh_3)_4$

A solution of PPh_3 (1-2 equivalents), the metal carbonyl compound (1 equivalent) ($W(CO)_6$, $Fe(CO)_5$, $CpFe(CO)_2I$, $Re(CO)_5(CH_3)$, $CpMn(CO)_3$, $Re_2(CO)_{10}$ or $Os_3(CO)_{12}$) and $Pt(PPh_3)_4$ (0.1 equivalent) were brought to reflux in 50 mL of benzene under an N_2 atmosphere. The reactions were monitored by changes in the IR spectra (2200-1600 cm^{-1}). At the end of the reaction (as established by the disappearance of the starting material), the solution was cooled to room temperature and the solvent removed under vacuum. The residue dissolved in CH_2Cl_2 was then passed through a silica-gel column (2.5 x 15 cm) using 1:1 CH_2Cl_2/hexanes as the eluant. The PPh_3-substituted products were collected. Recrystallization from CH_2Cl_2/hexanes gave the isolated products (% yields in Table 1) which were identified by their IR and ^1H NMR spectra (Table I). The catalyst, $Pt(PPh_3)_4$, was recovered. Also shown in Table I are results of control reactions where no Pt(0) catalyst was used.

Reaction of metal carbonyls with ligands in the presence of $Pt(dba)_2$

A 50 mL benzene solution containing a donor ligand (PPh_3, PPh_2Me, dppe, $P(OMe)_3$, or norbornadiene) (usually 1.5 equivalents), a metal carbonyl ($Fe(CO)_5$, or $CpFe(CO)_2I$) (1 equivalent) and $Pt(dba)_2$ (0.1 equivalent) was refluxed in a Schlenk flask. The reaction was monitored by IR spectroscopy (2200-1600 cm^{-1}), and heating was continued until the reaction had gone to completion. The solvent was removed in vacuum; the residue dissolved in CH_2Cl_2 was chromatographed (2.5 x 15 cm) on silica-gel using 1:1 CH_2Cl_2/hexanes as the eluent. The products were recrystallized from CH_2Cl_2/hexanes.

RESULTS AND DISCUSSION

The substitution of one CO ligand in a variety of metal carbonyl complexes by PPh_3 is catalyzed by $Pt(PPh_3)_4$ (eq 1) in refluxing benzene.

$$M_x(CO)_y + PPh_3 \xrightarrow[\text{benzene}]{Pt(PPh_3)_4} M_x(CO)_{y-1}(PPh_3) + CO \qquad (1)$$

where $M_x(CO)_y$ = $W(CO)_6$, $Fe(CO)_5$, $CpFe(CO)_2I$, $Re(CO)_5(CH_3)$, $Re_2(CO)_{10}$, and $Os_3(CO)_{12}$.

As summarized in Table 1, the products are isolated in 70-98% yields and the $Pt(PPh_3)_4$ catalyst may be recovered nearly quantitatively. Under the conditions of the reactions, but in the absence of the catalyst, there is essentially no reaction. Only the mono-phosphine-substituted complexes are obtained even when two equivalents of PPh_3 are used in the reactions, as for $Fe(CO)_5$ and $CpFe(CO)_2I$. Of the metal carbonyls studied, only $CpMn(CO)_3$ failed to undergo $Pt(PPh_3)_4$-catalyzed substitution. $CpMn(CO)_3$ is quite inert to thermal substitution in the absence of catalyst [16], and attempted PdO-catalyzed [9d] substitution was also unsuccessful.

The reaction between $Re_2(CO)_{10}$ and PPh_3 in refluxing xylene for 24 h yields $Re_2(CO)_8(PPh_3)_2$ and mer-trans-$HRe(CO)_3(PPh_3)_2$ as the main products [17]. The reaction of $Re_2(CO)_{10}$ with PMe_2Ph is reported [18] to yield mixtures of $Re_2(CO)_9(PMe_2Ph)$ and $Re_2(CO)_8(PMe_2Ph)_2$. The $Cp_2Fe_2(CO)_4$-

Table 1. Experimental conditions for the reactions of metal carbonyls with PR_3 ligands in the presence of $Pt(PPh_3)_4$ or $Pt(dba)_2$ catalysts

Metal Carbonyl	Ligands	Catalyst	Mole ratio[a]	Products	Pt(0) Catalyzed		Uncatalyzed	
(mmole)	(L)				Time	% Yield	Time	Results
$W(CO)_6$ (2.5 mmole)	PPh_3	$Pt(PPh_3)_4$	1:1:0.1	$W(CO)_5(PPh_3)$[b]	4 d	92	4 d	NR[c]
$Fe(CO)_5$ (2.5 mmole)	PPh_3	$Pt(PPh_3)_4$	1:2:0.1	$Fe(CO)_4(PPh_3)$[d]	5 h	98	19 h	[e]
	PPh_3	$Pt(dba)_2$	1:1.5:0.1	$Fe(CO)_4(PPh_3)$[d]	7 h	81		
	$PPhMe_2$	$Pt(dba)_2$	1:2:0.1	$Fe(CO)_4(PPhMe_2)$	1.5 h	79%	1.5	NR

[a]Metal carbonyl:PR_3:catalyst.

[b]Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. J. Am. Chem. Soc. 1961, 83, 3200.

[c]NR = no reaction.

[d]Clifford. A. F.; Mukherjee, A. K. Inorg. Synth. 1966, 8, 185.

[e]Without catalyst, only trace of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ along with $Fe(CO)_5$ are observed.

Table 1. Continued

Metal Carbonyl (mmole)	Ligands (L)	Catalyst	Mole ratio[a]	Products	Pt(0) Catalyzed		Uncatalyzed	
					Time	% Yield	Time	Results
	dppe	$Pt(dba)_2$	1:1.5:0.1	-----	8 h	NR		
	$P(OMe)_3$	$Pt(dba)_2$	1:2:0.1	-----	17 h	NR		
	NBD	$Pt(dba)_2$	1:2:0.1	-----	17 h	NR		
$CpFe(CO)_2I$ (0.50 mmol)	PPh_3	$Pt(PPh_3)_4$	1:1:0.1	$CpFe(CO)(PPh_3)I$[f]	50 min	87	24 h	NR
	PPh_3	$Pt(dba)_2$	1:1.5:0.1	$CpFe(CO)(PPh_3)I$[f]	50 min	85		
	$P(OMe)_3$	$Pt(dba)_2$	1:2:0.1	$CpFe(CO)[P(OMe)_3]I$[f]	30 min	91	30 min	[g]
	dppe	$Pt(dba)_2$	1:1.5:0.1	$CpFe(dppe)I$[h]	1 h	84	1 h	[i]

[f]a. Brown, D. A.; Lyons, H. J.; Manning, A. R.; Rowley, J. M. Inorg. Chim. Acta 1969, 3, 346. b. Brown, D. A.; Lyons, H. J.; Manning, A. R. Inorg. Chim. Acta 1970, 4, 428. c. Haines, R. J.; DuPreez, A. L.; Marais, L. L. J. Organomet. Chem. 1971, 28, 405.

[g]Eighty-three percent of $CpFe(CO)_2I$ was unreacted.

[h]Green, M. L. H.; Whitely, R. N. J. Chem. Soc. (A), 1971, 1943.

[i]Eighteen percent of $CpFe(CO)_2I$ was unreacted.

Table 1. Continued

Metal Carbonyl (mmole)	Ligands (L)	Catalyst	Mole ratio[a]	Products	Pt(0) Catalyzed Time	Pt(0) Catalyzed % Yield	Uncatalyzed Time	Uncatalyzed Results
$Re(CO)_5(CH_3)$ (10.30 mmol)	PPh_3	$Pt(PPh_3)_4$	1:1:0.1	$Re(CO)_4(PPh_3)(CH_3)$[j]	17 h	86	24 h	NR
$Re_2(CO)_{10}$ (0.60 mmol)	PPh_3	$Pt(PPh_3)_4$	1:1:0.1	$Re_2(CO)_9(PPh_3)$[k]	2 d	72	2 d	NR
$Os_3(CO)_{12}$ (0.20 mmol)	PPh_3	$Pt(PPh_3)_4$	1:1:0.1	$Os_3(CO)_{11}(PPh_3)$[l]	5 min	98	2 h	NR
$CpMn(CO)_3$ (2.50 mmol)	PPh_3	$Pt(PPh_3)_4$	1:1:0.1	-----	3d	NR		

[j]McKinney, R. J.; Kaesz, H. D. J. Am. Chem. Soc. 1975, 97, 3066.

[k]Dewitt, D. G.; Fawcett, J. P.; Pöe, A. J. Chem. Soc., Dalton Trans. 1976, 528.

[l]Bradford, C. W.; van Bronswijk, W.; Clark, R. J. H.; Nyholm, R. S. J. Chem. Soc. (A) 1970, 2889.

catalyzed [6d] substitution of $Re_2(CO)_{10}$ with PPh_3 was also unsuccessful. However, the present method gives $Re_2(CO)_9(PPh_3)$ in 72% isolated yield.

The reaction of $Os_3(CO)_{12}$ with PMe_3 causes extensive cluster fragmentation [19] while the Na-BPK method provides poor yields of di- and tri-substituted products [4a]. However, the $Pt(PPh_3)_4$ catalyst affords a high yield (98%) of the mono-substituted product, $Os_3(CO)_{11}(PPh_3)$, in only 5 mins. The $Pt(PPh_3)_4$-catalyzed reaction of $Re(CO)_5(CH_3)$ and PPh_3 gives only $Re(CO)_4(PPh_3)(CH_3)$. This product had previously [20] been prepared from the reaction of $Re(CO)_4(PPh_3)(Br)$ with MeLi.

The mechanism (Scheme I) of reaction (1) has not been studied in detail, but may involve electron transfer with the formation of a labile 19-electron metal carbonyl radical intermediate, as has been suggested for other [21] catalyzed metal carbonyl substitution reactions. This general type of mechanism for reaction (1) is supported by the inhibition of the reaction of $CpFe(CO)_2I$ (0.16 mmol) with PPh_3 (0.16 mmol) and $Pt(PPh_3)_4$ (0.016 mmol) by galvinoxyl (0.008 mmol). In refluxing benzene, 58% of the $CpFe(CO)_2I$ is unreacted even after 4 h, whereas the reaction is complete in 50 min in the absence of galvinoxyl. The first step in the mechanism probably involves PPh_3 dissociation from $Pt(PPh_3)_4$ to give $Pt(PPh_3)_3$ which is known to occur in benzene solution [22]. Then, electron-transfer from the $Pt(PPh_3)_3$ to the metal carbonyl would generate a labile radical intermediate which would undergo rapid CO substitution by the PPh_3 [23]. Electron transfer from the $M_x(CO)_{y-1}L^-$ radical then gives the $M_x(CO)_{y-1}L$ product and the reactive $M_x(CO)_y^-$ which continues the catalytic chain.

Scheme I

$$Pt(PPh_3)_4 \longrightarrow Pt(PPh_3)_3 + PPh_3$$

$$Pt(PPh_3)_3 + M_x(CO)_y \longrightarrow Pt(PPh_3)_3^{+\bullet} + M_x(CO)_y^{-\bullet}$$

$$M_x(CO)_y^{-\bullet} + PPh_3 \longrightarrow M_x(CO)_{y-1}(PPh_3)^{-\bullet} + CO$$

$$M_x(CO)_{y-1}(PPh_3)^{-\bullet} + M_x(CO)_y \longrightarrow M_x(CO)_{y-1}(PPh_3) + M_x(CO)_y^{-\bullet}$$

It has been noted that only mono-substitution occurs in reaction (1). In terms of the mechanism, this is likely to be the case because the mono-substituted $M_x(CO)_{y-1}L$ products are more electron-rich than $M_x(CO)_y$ and would be poorer acceptors of an electron from the Pt(0) catalyst. Likewise, the catalyzed substitutions of all of the complexes should depend on the electron accepting abilities of the complexes. Those which are likely to be the best acceptors will have the lowest electron density as measured by their high ν(CO) force constants. Thus, $Pt(PPh_3)_4$ catalyzes CO substitution in the following complexes with relatively high ν(CO) force constants (given in parentheses): $Fe(CO)_5$ (17.6 and 17.0 mdynes/Å) [24a], $W(CO)_6$ (16.56 mdynes/Å) [24a], $CpFe(CO)_2I$ (16.45 mdynes/Å) [24b], $Re(CO)_5(CH_3)$ (15.97 and 16.87 mdynes/Å) [24a], $Re_2(CO)_{10}$ (15.92 and 16.57 mdynes/Å) [24c], and $Os_3(CO)_{12}$ (16.53 and 16.79 mdynes/Å) [24d]. All of the complexes which react according to eq 1 have ν(CO) force constants greater than 16.4 mdynes/Å, in contrast to the unreactive $CpMn(CO)_3$ whose low k_{CO} value (15.6 mdynes/Å) [24a] indicates that it is relatively electron-rich and would be a poor electron acceptor.

Instead of using $Pt(PPh_3)_4$ as the catalyst in reaction (1), it is also possible to use $Pt(dba)_2$ which under the conditions of the reaction with excess PPh_3 is converted to $Pt(PPh_3)_2(dba)$ [14]. Thus, the reaction of $Fe(CO)_5$, PPh_3, and a catalytic amount of $Pt(dba)_2$ in refluxing benzene gives (Table 1) an 81% yield of $Fe(CO)_4(PPh_3)$. Similarly, the $Pt(dba)_2$-catalyzed reaction of $CpFe(CO)_2I$ with PPh_3 gives $CpFe(CO)(PPh_3)(I)$. The successful use of $Pt(dba)_2$ as a catalyst for the substitution of CO by PPh_3 suggests that other monodentate phosphines could be used in analogous reactions. Indeed, $Pt(dba)_2$ does catalyze the reaction of $Fe(CO)_5$ and $PPhMe_2$ to give $Fe(CO)_4(PPhMe_2)$ and the reaction of $CpFe(CO)_2I$ and $P(OMe)_3$ to give $CpFe(CO)[P(OMe)_3](I)$. The reaction of $CpFe(CO)_2I$ and $Ph_2PCH_2CH_2PPh_2$(dppe) to produce CpFe(dppe)I in the presence of $Pt(dba)_2$ is complete within 1 h, and the isolated yield is 84%. Without $Pt(dba)_2$, the reaction is not complete (18% of $CpFe(CO)_2I$ remained unreacted) under the same conditions. There was no observed $Pt(dba)_2$ catalysis of the reactions of $Fe(CO)_5$ with dppe, $P(OMe)_3$ or 2,5-norbornadiene(NBD), which suggests that the method may be limited to monodentate phosphines.

CONCLUSION

There are several attractive features of the $Pt(PPh_3)_4$-catalyzed method of substituting a CO ligand in metal carbonyls by PPh_3: (a) The reaction cleanly provides mono-substituted products in high yields (70-98%). (b) The catalyst can be recovered almost quantitatively at the end of the experiment. (c) For clusters which tend to fragment under other conditions, the $Pt(PPh_3)_4$ method yields the intact clusters. (d) k_{CO} values are helpful for predicting metal carbonyl complexes to which the method can be applied. The substitution of one CO in $Fe(CO)_5$ and $CpFe(CO)_2I$ by PPh_3 and/or PMe_2Ph is also catalyzed by $Pt(dba)_2$, suggesting that $Pt(dba)_2$ may be used more generally to catalyze monodentate phosphine substitution of metal carbonyls.

Acknowledgment

We appreciate the support of this research by the National Science Foundation (grant nos. CHE-8401844 and CHE-8719744).

REFERENCES

1. a. Clifford, A. F.; Mukherjee, A. K. Inorg. Chem. 1963, 2, 151. b. Cotton, F. A.; Parish, R. V. J. Chem. Soc. 1960, 1440.

2. Albers, M. O.; Coville, N. J. Coord. Chem. Rev. 1984, 53, 227.

3. a. Shvo, Y.; Hazum, E. J. Chem. Soc., Chem. Comm. 1975, 829. b. Koelle, U. J. Organomet. Chem. 1978, 155, 53. c. Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I. Inorg. Chem. 1980, 19, 1277. d. Luh, T.-Y. Coord. Chem. Rev. 1984, 60, 255.

4. a. Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. J. Chem. Soc., Chem. Commun. 1982, 442. b. Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Snow, M. R. J. Organomet. Chem. 1982, 235, 83. c. Butts, S. B.; Shriver, D. F. J. Organomet. Chem. 1979, 169, 191.

5. Bruce, M. I. Coord. Chem. Rev. 1987, 76, 1.

6. a. Coville, N. J.; Albers, M. O.; Singleton, E. J. Chem. Soc., Dalton Trans. 1983, 947. b. Coville, N. J.; Albers, M. O.; Ashworth, T. V.; Singleton, E. J. Chem. Soc., Chem. Commun. 1981, 408. c. Coville, N. J.; Darling, E. A. J. Organomet. Chem. 1984, 277, 105. d. Albers, M. O.; Coville, N. J.; Singleton, E. J. Organomet. Chem. 1982, 232, 261. e. Harris, G. W.; Albers, M. O.; Boeyens, J. C. A.; Coville, N. J. Organometallics 1983, 2, 609. f. Aime, S.; Botta, M.; Gobetto, R.; Osella, D. Inorg. Chim. Acta 1986, 115, 129.

7. a. Coville, N. J. J. Organomet. Chem. 1980, 190, C84. b. Coville, N. J. J. Organomet. Chem. 1981, 218, 337.

8. a. Albers, M. O.; Coville, N. J.; Singleton, E. J. Chem. Soc., Dalton Trans. 1982, 1069. b. J. Organomet. Chem. 1980, 199, 55; c. J. Organomet. Chem. 1981, 217, 385; d. Albers, M. O.; Coville, N. J.; Ashworth, T. V.; Singleton, E.; Swanepoel, H. E. J. Chem. Soc., Chem. Commun. 1980, 489.

9. a. Albers, M. O.; Coville, N. J.; Singleton, E. J. Chem. Soc., Chem. Commun. 1982, 96. b. Coville, N. J.; Albers, M. O. Inorg. Chim. Acta 1982, 65, L7. c. Albers, M. O.; Coville, N. J.; Singleton, E. J. Organomet. Chem. 1982, 234, C13. d. Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. J. Organomet. Chem. 1983, 255, 87.

10. Aime, S.; Botta, M.; Gobetto, R.; Osella, D. Organometallics 1985, 4, 1475.

11. King, R. B. Organometallic Syntheses; Academic Press: New York 1965; Vol. 1, p. 175-6.

12. Hieber, W.; Braun, G.; Beck, W. Chem. Ber. 1960, 93, 901.

13. Ugo, R.; Cariati, F.; La Monica, G. Inorg. Syn. 1968, 11, 105.

14. Cherwinski, W. J.; Johnson, B. F. G.; Lewis, J. J. Chem. Soc., Dalton Trans. 1974, 1405.

15. Bradford, C. W.; Nyholm, R. S. Chem. Commun. 1967, 384.

16. Caulton, K. G. Coord. Chem. Rev. 1981, 38, 1.

17. Cox, D. J.; Davis, R. J. Organomet. Chem. 1980, 186, 339.

18. Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. J. Chem. Soc., Dalton Trans. 1985, 2277.

19. Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. Inorg. Chem. 1985, 24, 2777.

20. McKinney, R. J.; Kaesz, H. D. J. Am. Chem. Soc. 1975, 97, 3066.

21. Geiger, W. E.; Connelly, N. G. Adv. Organomet. Chem. 1985, 24, 87; Geiger, W. E.; Connelly, N. G. Adv. Organomet. Chem. 1984, 23, 1.

22. Birk, J. P.; Halpern, J.; Pickard, A. L. Inorg. Chem. 1968, 7, 2672.

23. a. Arewgoda, C. M.; Robinson, B. H.; Simpson, J. J. Chem. Soc., Chem. Commun. 1982, 284; b. Arewgoda, M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. J. Am. Chem. Soc. 1982, 104, 5633.

24. a. Avanzino, S. C.; Bakke, A. A.; Chen, H. W.; Donahue, C. J.; Jolly, W. L.; Lee, T. H.; Ricco, A. J. Inorg. Chem. 1980, 19, 1931. b. Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. J. Am. Chem. Soc. 1972, 94, 3406. (c) Flitcroft, N.; Huggins, D. K.; Kaesz, H. D. Inorg. Chem. 1964, 3, 1123. d. Battiston, G. A.; Bor, G.; Dietler, U. K.; Kettle, S. F. A.; Rossetti, R.; Sbrignadello, G.; Stanghellini, P. L. Inorg. Chem. 1980, 19, 1961.

SUMMARY

$Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$ and $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ are synthesized from the reaction of $Os_3(CO)_{12}$ and ethylene oxide in the presence of Br^-. $Fe(CO)_4(=\overline{COCH_2CH_2O})$ decomposes with evolution of CO_2 and ethylene. It also reacts with oxidizing agent, Me_3NO or O_2, to produce ethylene carbonate and reacts with H_2 gas to give 1,3-dioxolane.

In the reactivity studies of $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$, it shows that CO is replaced by phosphine or hydrotris(pyrazolyl)borate ligands, the Br is replaced by a methyl and the NH group is replaced by $N\text{-}CH_3$.

The reactions between metal carbonyls and phosphines in refluxing benzene are catalyzed by $Pt(PPh_3)_4$ and $Pt(dibenzylideneacetone)_2$. This method provides a convenient (short reaction time and recovery of catalysts), high yields (72-98%) route to only mono-substituted complexes.

ACKNOWLEDGMENTS

I would like to express my sincere appreciation to Dr. Angelici for his patient guidance and continuous encouragement during the course of my graduate education. I also want to thank the members of the A-team and all my friends here in Ames for their great friendship. I wish to thank Dr. James H. Espensen, Dr. Robert E. McCarley, Dr. Richard C. Larock and Dr. Glenn L. Schrader for their serving on my Ph.D. committee and their review of this dissertation.

I am especially grateful to my parents and my sister and brother for their love, support and confidence. I also wish to thank Weir-Mirn, my husband, for his encouragement, understanding and moral support during these years. Special thanks to Mrs. Nancy Qvale for typing this manuscript and her enthusiasm in doing this.