Organometallics **1988,** *7,* 2475–2479

(δ 0.94 (J_{PH} = 9.3 Hz, J_{HgH} = 35.4 Hz)) resonances were coupled to phosphorus as well as to mercury, showing that all of the ligands were still bonded to the osmium (see Experimental Section for full details).

The ^{1}H NMR and IR data were consistent, by the same arguments that were used to identify the previous intermediates, with the species being of osmium(IV). The isolation of this intermediate has shown that electrophilic cleavage of the osmium–carbon bond of the complex Cp*Os(CO)(PMe$_2$Ph)Me with HgBr$_2$ proceeds via oxidative addition of HgBr$_2$ to the osmium(II) methyl complex to form the osmium(IV) complex (eq 9). The intermediate, of a type previously proposed for mercuric halide cleavages of complexes of the type CpFe(CO)$_2$R (R = alkyl),[6,7] has thus been confirmed, and by comparison with this isolated intermediate, the intermediates identified spectroscopically for other electrophilic cleavages of these osmium alkyl complexes are of the same type (osmium(IV) species).

$$\mathrm{Cp^*Os(CO)(PMe_2Ph)Me + HgBr_2 \rightarrow [Cp^*Os(CO)(PMe_2Ph)(Me)(HgBr)]^+Br^- \rightarrow Cp^*Os(CO)(PMe_2Ph)Br + MeHgBr} \tag{9}$$

Summary and Conclusions. With few exceptions, reactions of osmium alkyl complexes of the type Cp*Os(CO)LR (L = CO, PMe$_2$Ph; R = Me, Et, *i*-Pr, CH$_2$Ph) with the electrophiles CF$_3$CO$_2$H, Br$_2$, and HgBr$_2$ all proceed as expected by comparison to previous work done on similar systems.[6–10,38,40] In most cases, spectroscopic evidence for the intermediates, previously proposed for these reactions but not identified, was found. The reactions all proceed via two-electron oxidation processes to give formally osmium(IV) intermediates of the type [Cp*Os(CO)L(R)(E)]$^+$X$^-$, where the electrophile is represented as EX. In addition, for the reaction of Cp*Os(CO)(PMe$_2$Ph)Me with HgBr$_2$, the intermediate was isolated.

In general, the oxidized intermediates were more stable when L = PMe$_2$Ph than when L = CO and when R = Me or Et than when R = *i*-Pr or CH$_2$Ph. It is perhaps not surprising that the phosphine-substituted osmium(IV) complexes are the more stable, as the better electron-donating phosphine should more readily stabilize the higher oxidation state. However, the intermediates that would be formed during cleavage of the isopropyl and benzyl complexes were not observed in any of the reactions. Thus it would seem that the intermediates for R = *i*-Pr and CH$_2$Ph were not as stable as those of the methyl and ethyl analogues, perhaps because of lower osmium–carbon bond energies.[43]

Acknowledgment. This research was made possible by financial assistance from the Natural Sciences and Engineering Research Council of Canada in the form of scholarships to L.J.J. and operating grants to M.C.B. We are also indebted to the International Nickel Co. and Johnson Matthew for loans of osmium salts and to L. G. Sturgeoff and W. A. G. Graham for information concerning unpublished synthetic procedures.

Registry No. Cp*Os(CO)$_2$Br, 81554-89-4; Cp*Os(CO)$_2$Me, 102149-67-7; Cp*Os(CO)$_2$Et, 116669-97-7; Cp*Os(CO)$_2$(*i*-Pr), 116669-98-8; Cp*Os(CO)$_2$CH$_2$Ph, 116669-99-9; Cp*Os(CO)(PMe$_2$Ph)Br, 107087-80-9; Cp*Os(CO)(PMe$_2$Ph)Me, 107087-79-6; Cp*Os(CO)(PMe$_2$Ph)Et, 116670-00-9; Cp*Os(CO)(PMe$_2$Ph)(*i*-Pr), 116670-01-0; Cp*Os(CO)(PMe$_2$Ph)CH$_2$Ph, 116670-02-1; Cp*Os(CO)(PMe$_2$Ph)(OCOCF$_3$), 116670-03-2; [Cp*Os(CO)(PMe$_2$Ph)(Me)(HgBr)]PF$_6$, 107087-83-2; [Cp*Os(CO)(PMe$_2$Ph)(Me)H](CF$_3$CO$_2$), 116670-05-4; [Cp*Os(CO)(PMe$_2$Ph)(Me)Br]Br, 107333-51-7; [Cp*Os(CO)$_2$(Me)(HgBr)]Br, 116670-06-5; [Cp*Os(CO)$_2$(Et)(HgBr)]Br, 116724-45-9; [Cp*Os(CO)(PMe$_2$Ph)(Me)(HgBr)]Br, 107087-81-0; [Cp*Os(CO)(PMe$_2$Ph)(Et)(HgBr)]Br, 116670-07-6.

---

(43) Halpern, J. *Acc. Chem. Res.* **1982,** *15,* 238.

Mechanism of Carbonyl "Insertion" Reactions of the Compounds *cis*-MMeX(CO)$_2$(PMe$_3$)$_2$ (M = Fe, Ru; X = I, CN). Stereochemistry at the Metal Centers

G. Cardaci,* G. Reichenbach, and G. Bellachioma

Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

Berend Wassink and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6

Received March 8, 1988

Reactions of the compounds *cis*-MMeX(CO)$_2$(PMe$_3$)$_2$ (M = Fe, Ru; X = I, CN) with ^{13}CO, of the compounds *cis*-MMeX(^{13}CO)$_2$(PMe$_3$)$_2$ with ^{12}CO, and of selectively labeled compounds *cis*-MMeX(^{12}CO)(^{13}CO)(PMe$_3$)$_2$ with ^{13}CO are monitored by IR and variable-temperature ^{13}C NMR spectroscopy. In all cases, analyses of the reaction products indicate that the reactions involve a "migratory insertion" process in which the methyl group migrates to a cis carbonyl group. There is no evidence for a mechanism involving formal carbon monoxide migration to the methyl site.

Introduction

The mechanism of carbon monoxide insertion into the metal–carbon σ-bond (eq 1) has been extensively studied,

$$\mathrm{MR(CO)L_n + L' \rightarrow M(COR)L_nL'} \tag{1}$$

as the reaction constitutes a key step in many catalytic processes.[1,2] Many studies of the stereochemistry at the α-carbon atom of the alkyl group R have been carried out, and it has been found that reactions as in (1) generally

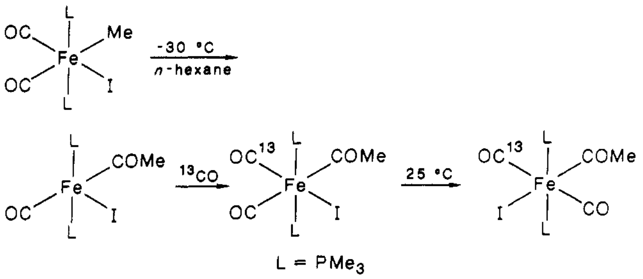
---

(1) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977,** *16,* 299.

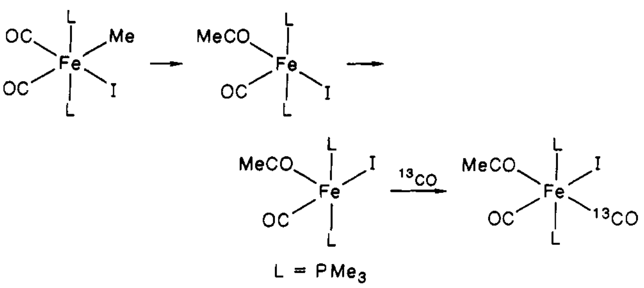
(2) Wojcicki, A. *Adv. Organomet. Chem.* **1973,** *11,* 87.

0276-7333/88/2307-2475$01.50/0

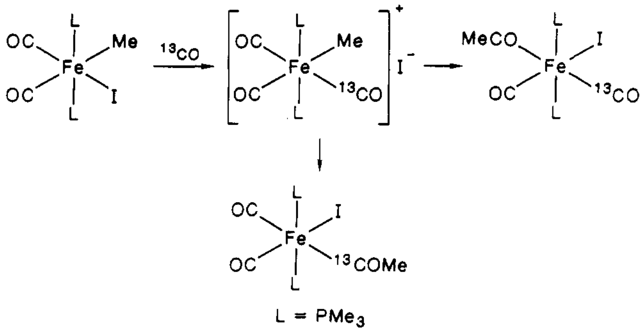
Scheme I



Scheme II



Scheme III



involve retention of configuration at the carbon atom.[3,4] In contrast, investigations of the stereochemistry at various types of metal centers have resulted in a diversity of conclusions and in fact suggest that two pathways for the reaction are possible. Thus the reversible carbonylation of $MeMn(CO)_5$ with ^{13}CO has been monitored by both IR[5] and ^{13}C NMR[6] spectroscopy, and it is clear that the "insertion" process of this system involves migration of the methyl group to a cis CO ligand. The migratory insertion reaction has also been considered theoretically.[7-10]

In recent years, however, two apparent examples of formal CO migration have been reported. For instance, two groups have shown that carbonylation reactions of resolved, chiral complexes of the type CpFe(CO)LR can proceed via both formal alkyl and formal CO migration.[11,12] While the former probably involves the type of migratory insertion envisaged above for the $MeMn(CO)_5$ system, a satisfactory understanding of the occurrence of CO migration has not yet been presented.

The second example of apparent CO migration involves compounds of the type $MMeX(CO)_2(PMe_3)_2$ (M = Fe, Ru; X = I, CN),[13] which have been claimed by Pańkowski and Bigorgne to react with ^{13}CO as shown in Scheme I for the iodoiron compound. At room temperature, the cis isomer shown in Scheme I isomerizes to the thermodynamically more stable trans isomer, as shown. However, as formation of the cis isomer seemed to involve initial migration of the CO trans to the iodine (CO) followed by coordination of labeled CO at the site cis to the acetyl group, it was concluded that the reaction involves formal CO migration.

Identification of the structure of the cis intermediate, however, was based solely on its IR spectra in the carbonyl stretching region, an approach which has subsequently been shown to provide ambiguous interpretations. Thus, in two previous, complementary studies,[14,15] we have investigated the carbonylation of the compounds $FeMeX(CO)_2(PMe_3)_2$ (X = I, CN, NCS) in polar and nonpolar solvents by IR and NMR spectroscopy and the carbonylation of $FeMeI(CO)_2(PMe_3)_2$ in methylene chloride by variable-temperature ^{13}C NMR spectroscopy. We concluded not only that the reactions with ^{13}CO are much more complicated than is suggested by Scheme I, but also that they involve only formal methyl migration.

Thus in nonpolar solvents, reaction of the iodo compound has been shown to involve initial methyl migration followed by rapid isomerization of the square-pyramidal intermediate (Scheme II). The incoming CO then coordinates to the vacant site trans to the acetyl group to give the isotopomer of the cis complex suggested in Scheme I. This mechanism also appears to apply to the analogous cyanoiron compound, even in polar solvents. In all cases involving ^{13}CO, secondary reactions can lead to multiple labeling.

In polar solvents, the iodo compound reacts with ^{13}CO via an ionic intermediate, as in Scheme III. The methyl group of the ionic intermediate can migrate to either of the cis carbonyl groups, as shown, giving rise to products labeled in both the CO trans to the acetyl and in the acetyl group when ^{13}CO is used. The first step, involving substitution of iodide by ^{13}CO, is reversible, and thus labeled starting material is also formed (as are two labeled trans acetyl products when the temperature is raised). The cyano compound does not appear to react in this way, even in polar solvents, presumably because the cyanide ion is a poorer leaving group than is the iodide ion.

In order to gain a more complete picture of the mechanism(s) of reactions of the type shown in Scheme I, we have now investigated by IR and ^{13}C NMR spectroscopy the carbonylation of $FeMeI(CO)_2(PMe_3)_2$ in the nonpolar solvent toluene-d_8. The IR study by Pańkowski and Bigorgne[13] had utilized n-hexane as a solvent while our earlier studies of the same compound had utilized the more polar methylene chloride.[14,15] As pointed out above, solvent effects can influence the course of the reaction, and it was clearly of interest to carry out a combined IR–NMR investigation of the iodo system in a nonpolar solvent. We have used toluene because $FeMeI(CO)_2(PMe_3)_2$ is not sufficiently soluble in n-hexane for NMR studies. We have also extended, utilizing ^{13}C NMR spectroscopy, previous studies of the carbonylation of $RuMeX(CO)_2(PMe_3)_2$ (X = I, CN),[13,14] and we report here the results of these experiments as well.

---

(3) Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

(4) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814.

(5) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *16*, 101.

(6) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

(7) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

(8) Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572.

(9) Ziegler, T.; Versluis, L.; Tschinke, V. *J. Am. Chem. Soc.* **1986**, *108*, 612.

(10) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136.

(11) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853 and references therein.

(12) Brunner, H.; Hammer, B.; Bernal, I.; Draux, M. *Organometallics* **1983**, *2*, 1595.

(13) Pańkowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1983**, *251*, 333.

(14) Cardaci, G.; Reichenbach, G.; Bellachioma, G. *Inorg. Chem.* **1984**, *23*, 2936.

(15) Wright, S. C.; Baird, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 6899.

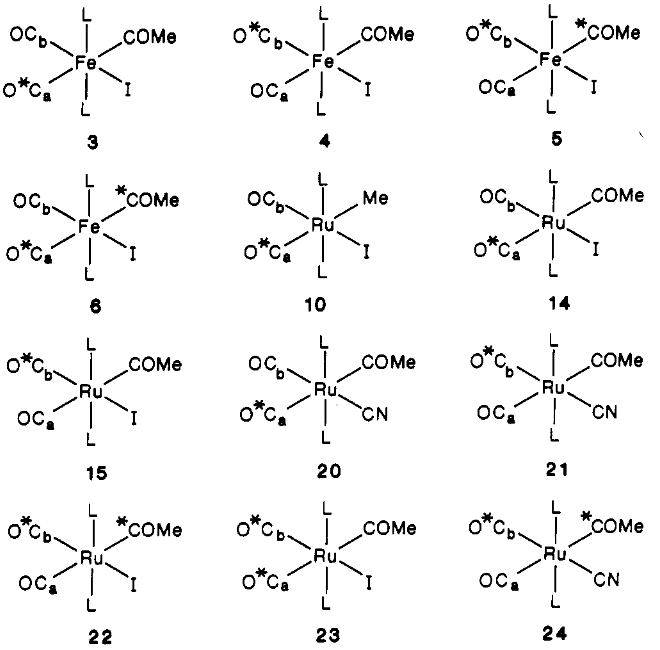


Figure 1. Structures of the partially labeled compounds (L = PMe$_3$, *CO = ^{13}CO).

All complexes discussed in this work have the two PMe$_3$ ligands mutually trans. Unless otherwise indicated, all dicarbonyl complexes have the two CO ligands mutually cis; CO groups trans to methyl (or acetyl) are denoted "a", while those trans to iodine (or cyanide, CO) are denoted "b". The structures of all the partially labeled complexes prepared herein are shown in Figure 1.

Experimental Section

Solvents were purified following literature procedures.[16] The compounds FeMeI(CO)$_2$(PMe$_3$)$_2$ (1),[17] RuMeI(CO)$_2$(PMe$_3$)$_2$ (8),[18] and PMe$_3$[19] were prepared as described in the literature. IR spectra were recorded on Perkin-Elmer 983 IR and Bruker IFS-85 FTIR spectrometers and ^{13}C NMR spectra on a Bruker AM-400 NMR spectrometer. NMR samples were prepared by dissolving about 40 mg of sample in 0.5 mL of solvent maintained at the desired temperature. Carbonylation of an NMR sample involved passing CO (or ^{13}CO) through the solution for 10 s and then letting the sample stand for 5 min, all at the desired temperature. This procedure was repeated three times. IR and NMR data are listed in Tables I and II; all compounds were characterized where possible via comparisons of their spectral properties with data from the literature. Enriched ^{13}CO (99%) was purchased from MRC Mound and MSD Isotopes.

Preparation of Labeled Complexes. FeMeI(^{13}CO)$_2$(PMe$_3$)$_2$ (2). A solution of FeMeI(CO)$_2$(PMe$_3$)$_2$ (1) (0.25 g) in 10 mL of CH$_2$Cl$_2$, thermostated at 25 °C, was stirred with 40 mL of ^{13}CO for 24 h. The IR spectrum of the reaction solution at this point showed the presence of only partially labeled *trans*-Fe(COMe)I(CO)$_2$(PMe$_3$)$_2$, and the procedure was therefore repeated five times. The final IR spectrum showed that the solution now contained *trans*-Fe(^{13}COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$ enriched to the extent of 90%, and the solvent was removed under reduced pressure. The residue was dissolved in *n*-hexane and decarbonylated by refluxing under nitrogen for 1 h to give red crystals of the product, FeMeI(^{13}CO)$_2$(PMe$_3$)$_2$ (2).

Fe(COMe)I(CO)(^{13}CO)(PMe$_3$)$_2$ (3). A solution of 1 in *n*-hexane (20 mL, 5.1 × 10^{-2} Mm) was cooled to −30 °C and treated with 40 mL of ^{13}CO. An orange precipitate of the product formed immediately, whereupon the supernatant solution was removed by syringe and the product was dried at reduced pressure.

Table I. IR Data

compound	ν_{CO}	ν_{COMe}	ν_{CN}
FeMeI(CO)$_2$L$_2$ (1)[a]	1997.5, 1936.7		
FeMeI(^{13}CO)$_2$L$_2$ (2)[a]	1952.5, 1895.5		
Fe(COMe)I(CO)(^{13}CO)L$_2$ (3)[b]	1990.0, 1930.0	1586	
RuMeI(CO)$_2$L$_2$ (8)[c]	2022.0, 1954.0		
RuMeI(^{13}CO)$_2$L$_2$ (9)[c]	1974.5, 1909.5		
RuMeI(CO)(^{13}CO)L$_2$ (10)[a]	1999.5, 1935.5		
RuMeI(CO)(^{13}CO)L$_2$ (10)[b]	1998.0, 1932.5		
[RuMe(CO)$_3$L$_2$]BPh$_4$ (11)[c]	2114.0, 2044.0		
[RuMe(^{13}CO)$_3$L$_2$]BPh$_4$ (12)[c]	2065.0, 1999.0		
Ru(COMe)I(CO)$_2$L$_2$ (13)[c]	2040.0, 1978.0	1585	
Ru(COMe)I(CO)(^{13}CO)L$_2$ (14)[c]	2019.0, 1955.0	1583	
trans-Ru(COMe)I(CO)$_2$L$_2$[c]	2078.0, 1988.0	1596.5	
trans-Ru(^{13}COMe)I(^{13}CO)$_2$L$_2$[d]	1942.0	1568	
RuMeCN(CO)$_2$L$_2$ (17)[c]	2026.0, 1969.5		2121.0
RuMeI(^{13}CO)$_2$L$_2$ (18)[c]	1980.5, 1926.5		2120.0
Ru(COMe)CN(CO)$_2$L$_2$ (19)[c]	2044.5, 1995.0	1591	2125.0
Ru(^{13}COMe)CN(^{13}CO)$_2$L$_2$ (25)[c]	1999.5, 1950.5	1554.5	2123.0
trans-Ru(COMe)I(^{13}CO)$_2$L$_2$[c]	1944.5	1597.5	

[a] *n*-Hexane. [b] Toluene. [c] CH$_2$Cl$_2$. [d] Acetone.

RuMeI(CO)(^{13}CO)(PMe$_3$)$_2$ (10). A solution of 0.25 g of RuMeI(CO)$_2$(PMe$_3$)$_2$ (8) in 10 mL of CH$_2$Cl$_2$ was stirred at room temperature for 24 h under 40 mL of ^{13}CO. This procedure was repeated three times, after which the IR spectrum of the solution indicated the formation of *trans*-Ru(COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$. The latter was decarbonylated under a flow of nitrogen gas at room temperature to form a solution of RuMeI(CO)(^{13}CO)(PMe$_3$)$_2$ (10). Only small quantities of *trans*-Ru(^{13}COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$ were observed, and thus this method cannot be used to prepare RuMeI(^{13}CO)$_2$(PMe$_3$)$_2$ (9).

[RuMe(CO)$_3$(PMe$_3$)$_2$]BPh$_4$ (11). A flow of CO was passed through a solution of 2 g of RuMeI(CO)$_2$(PMe$_3$)$_2$ (8) in methanol for 2 h, and then excess NaBPh$_4$ was added. Slow precipitation of the desired product occurred. Anal. Calcd for C$_{34}$H$_{41}$BO$_3$P$_2$Ru: C, 60.45; H, 6.71. Found: C, 60.6; H, 6.75.

[RuMe(^{13}CO)$_3$(PMe$_3$)$_2$]BPh$_4$ (12). A solution of 0.35 g of [RuMe(CO)$_3$(PMe$_3$)$_2$]BPh$_4$ (11) in 20 mL of CH$_2$Cl$_2$ was stirred under 40 mL of ^{13}CO for 12 h at room temperature; the procedure was repeated six times to give the product.

RuMeI(^{13}CO)$_2$(PMe$_3$)$_2$ (9). A solution of 0.25 g of 12 in 20 mL of acetone was stirred with an excess of sodium iodide. Reaction was instantaneous, and after a few minutes, the solvent was removed under reduced pressure and the residue was extracted with benzene. The IR spectrum of the resulting solution indicated the presence of both 9 and the acetyl compound *trans*-Ru(^{13}COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$, and the latter was converted to 9 on refluxing the solution under nitrogen.

Ru(COMe)I(CO)(^{13}CO)(PMe$_3$)$_2$ (14). A solution of 90 mg of RuMeI(CO)$_2$(PMe$_3$)$_2$ (8) in 20 mL of *n*-hexane was cooled to −30 °C and stirred vigorously under 40 mL of ^{13}CO. A white solid precipitated, and the supernatant was removed by syringe. The solid was then dried and shown by IR spectroscopy (ν_{CO} = 2021, 1953.5 cm^{-1}; ν_{COMe} = 1616.5 cm^{-1}; Nujol mull) to be 14. Decarbonylation by a flow of nitrogen produced unenriched RuMeI(CO)$_2$(PMe$_3$)$_2$ (8).

RuMeCN(CO)$_2$(PMe$_3$)$_2$ (17) and RuMeCN(^{13}CO)$_2$(PMe$_3$)$_2$ (18). A solution of 1.14 g of [RuMe(CO)$_3$(PMe$_3$)$_2$]BPh$_4$ (11) in 20 mL of tetrahydrofuran was stirred with an excess of potassium cyanide at room temperature for 6 h. The solid material was removed by filtration, and an IR spectrum showed that the species in solution were RuMeCN(CO)$_2$(PMe$_3$)$_2$ (17) and *cis*-Ru(COMe)CN(CO)$_2$(PMe$_3$)$_2$ (19). The latter was decarbonylated to the former with a flow of nitrogen, and the solvent was removed under reduced pressure. The resulting white solid was recrystallized from CH$_2$Cl$_2$–hexane to give pure RuMeCN(CO)$_2$(PMe$_3$)$_2$ (17). Anal. Calcd for C$_{10}$H$_{21}$NO$_2$P$_2$Ru: C, 34.29; H, 6.04; N, 4.00. Found: C, 34.2; H, 6.06; N, 4.15. The same procedure was followed to prepare 18 from 12.

Ru(COMe)CN(CO)$_2$(PMe$_3$)$_2$ (19). A solution of 0.5 g of RuMeCN(CO)$_2$(PMe$_3$)$_2$ (17) in 20 mL of CH$_2$Cl$_2$ was treated with flowing carbon monoxide (unenriched). After 30 min, *n*-hexane

---

[16] Weissberger, A.; Proskauer, E. S. *Technique of Organic Chemistry*: Interscience: New York, 1955: Vol. VII.

[17] Pańkowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227.

[18] Cardaci, G. *J. Organomet. Chem.* **1987**, *323*, C10.

[19] Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

Table II. NMR Data

compd	^{13}C data (J_{CP}, Hz)			^{1}H data (J_{HP}, Hz)
	δ_{C_aO}	δ_{C_bO}	δ_{COMe}	δ_{M-Me}, δ_{COMe}
2[a]	208.0 (t) (15.6)	219.3 (t) (25.6)		not recorded
3[b]	208.6 (t) (10)			not recorded
4[a]		216.5 (t) (25)		not recorded
5[b]		216.5 (t) (24.5)	269.9	not recorded
6[a]	208.7 (t) (10)		270.1	not recorded
7[b]	~209.2	216.6 (br, t)	269.9	not recorded
9[a]	191.5 (t) (8)	198.6 (t) (12)		0.03 (t) (8)
10[a]	191.5 (t) (9)			0.00 (dt) (7.6) J_{HCO^a} = 0.8
12[a]	187.9 (t) (<5)	194.2 (t) (13)		1.13 (t)
14[a]	193 (t) (8.5)			2.53 (s)
16[a]	192.9 (dt) (<5) J_{C-OMe} = 26.5 Hz	194.3 (t) (11)	263 (dt) (11) J_{C-COMe} = 26.6 Hz	not recorded
18[a]	193.0 (t) (8)	200.2 (t) (11)		−0.43 (t) (8)
20[a]	194.8 (t) (8)			2.40 (s)
22[a]		194.4 (t) (11.5)	262.9 (t) (11)	2.53 (d) $J_{HCC{=}O}$ = 4.3 Hz
24[a]		195.7 (t) (11)	263.6 (t) (10.5)	not recorded
25[a]	194.8	195.7	264.1 (t) (11) J_{C-COMe} = 22 Hz	not recorded

[a] CD_2Cl_2. [b] Toluene.

was added and the solution was cooled to −20 °C to give a white precipitate of the product. Anal. Calcd for $C_{11}H_{21}NO_3P_2Ru$: C, 34.92; H, 5.60, N, 3.70. Found: C, 35.0; H, 5.45; N, 3.85.

Ru(COMe)CN(CO)(^{13}CO)(PMe$_3$)$_2$ (20). A solution of 0.1 g of RuMeCN(CO)$_2$(PMe$_3$)$_2$ in 10 mL of CH_2Cl_2 was stirred at room temperature for 20 min under 40 mL of ^{13}CO. An IR spectrum showed that **20** had formed. The solution did not change on heating to 35 °C and then standing for 48 h, but decarbonylation to unlabeled RuMeCN(CO)$_2$(PMe$_3$)$_2$ (17) was effected by a nitrogen flow at room temperature.

Results and Discussion

The structures of the partially labeled complexes synthesized in this work are shown in Figure 1. Relevant IR data are presented in Table I and ^{1}H and ^{13}C NMR data in Table II; assignments are based where possible on data for the compounds in the literature. Assignments of ^{13}CO resonances for the ruthenium complexes were made on the same basis that analogous assignments were previously made for the iron series.[14,15] Thus assignments were made for **12** on the basis of relative intensities, for the other compounds on the basis that trans influences will be a dominant factor both on the chemical shifts and on the coupling constants. Thus for both the iron and the ruthenium series of complexes, there is a set of ^{13}CO resonances to lower field with relatively small values of $^2J_{CP}$ and a set of resonances to higher field with relatively large values of $^2J_{CP}$. The former are to be assigned to the ^{13}CO trans to methyl or acetyl and the latter to the ^{13}CO trans to I, CN, or CO. We note that trans influences have a very significant effect on the ^{13}C–^{13}C coupling constants in the ruthenium complexes. Thus cis $^2J_{CO-CO}$ and cis $^2J_{CO-COME}$ are always <1 Hz, while trans $^2J_{CO-COMe} \approx$ 22–26 Hz. Similar trends have been noted elsewhere for $^2J_{P-P}$,[22] and thus these data strengthen the assignments.

(a) Iron Complexes. FeMeI(CO)$_2$(PMe$_3$)$_2$ (1) reacts with ^{13}CO in *n*-hexane at −30 °C to form *cis*-Fe(COMe)I(CO) (^{13}CO)(PMe$_3$)$_2$ (3), which precipitates as an orange solid but was characterized by its IR spectrum in toluene at −30 °C. To complement the IR study, a ^{13}C NMR study of the reactions of FeMeI(CO)$_2$(PMe$_3$)$_2$ (1) with ^{13}CO and of FeMeI(^{13}CO)$_2$(PMe$_3$)$_2$ (2) with enriched and unenriched carbon monoxide were carried out in toluene-d_8 at −40 °C. Assignments of the carbonyl resonances were based on previous work.[15] It was found that 1 reacts with ^{13}CO to give well-resolved resonances of the two isotopomers 3 and 4 in a 4:1 ratio. In the same way, 2 reacts with ^{13}CO to give somewhat poorly resolved (because of ^{13}C–^{13}C spin–spin coupling) resonances of Fe(^{13}COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$ (7) and with normal CO to give well-resolved resonances of the two isotopomers 5 and 6 in the ratio 4:1.

No indication that the incoming carbon monoxide ends up in the acetyl group was observed in any of the experiments, and thus the reactions do not involve the type of ionic intermediate that applies to the carbonylation of 1 in CH_2Cl_2[14,15] and is illustrated in Scheme III. The results are, however, consistent with those obtained for the isothiocyanato and cyano derivatives in CH_2Cl_2,[14] which also do not involve ionic intermediates. We do not feel that the small amounts of incoming CO which appear cis to the acetyl groups of the products in these reactions require that formal CO migration constitutes a minor pathway; the small amounts of the second isotopomer are more likely a result of dynamic square-pyramidal intermediates.

(b) Ruthenium Complexes. The compound RuMeI(CO)$_2$(PMe$_3$)$_2$ (8) reacts with carbon monoxide at −30 °C to give Ru(COMe)I(CO)$_2$(PMe$_3$)$_2$ (13), which isomerizes at 10 °C to the corresponding trans isomer. We note that similar observations have been made for the PMe$_2$Ph system studied by Mawby and co-workers.[21] The triply labeled compound Ru(Me^{13}CO)I(^{13}CO)$_2$(PMe$_3$)$_2$ (**16**) can be synthesized in the same way by treating RuMeI(^{13}CO)$_2$(PMe$_3$)$_2$ (9) with ^{13}CO at −30 °C, although the resonances were much broadened by ^{13}C–^{13}C spin–spin coupling. In this study, all reactions were carried at temperatures <−30 °C to avoid the cis–trans isomerization process.

The compound RuMeI(CO)$_2$(PMe$_3$)$_2$ (8) reacts with ^{13}CO in *n*-hexane at −30 °C to give *cis*-Ru(COMe)I(CO)(^{13}CO)(PMe$_3$)$_2$ (**14**), which precipitates as a white solid. The IR spectrum of a toluene solution of the solid at −30 °C exhibits ν_{CO} assignable to the monolabeled cis acetyl derivative[22] (Table I), while the ^{13}CO NMR spectrum shows that none of the isotopomer **15** is formed. Decarbonylation of a toluene solution under a nitrogen flow regenerates **8**. In a similar fashion, reaction of **9** with normal CO at −30 °C results in the formation only (by ^{13}CO NMR spectroscopy) of Ru(^{13}COMe)(CO)(^{13}CO)(PMe$_3$)$_2$ (**22**). In contrast, carbonylation of **8** with ^{13}CO in CH_2Cl_2

---

(20) Pregosin, P. *^{31}P and ^{13}C NMR of Transition Metal Complexes*; Springer-Verlag: New York, 1979.

(21) Barnard, C. F.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331.

(22) Braterman, P. S. *Metal Carbonyl Spectra*; Academic: London, 1979; pp 33–36.

at room temperature gives *trans*-Ru(COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$, which decarbonylates to give RuMeI(CO)(^{13}CO)(PMe$_3$)$_2$ (**10**) when nitrogen is bubbled through the solution. The latter reacts in turn with ^{13}CO at −40 °C to form Ru(COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$ (**23**).

As with reactions of **1** in *n*-hexane and toluene, discussed above, the reaction of **8** with ^{13}CO yields a product in which no labeling occurs in the acetyl resonance, and thus a mechanism as in Scheme II presumably applies rather than the ionic mechanism of Scheme III. This conclusion seems reasonable, assuming that the soft iodide dissociates less readily from ruthenium that from iron.

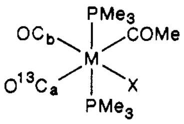
In contrast to the reactions of the iodo derivatives[21] but similar to the iron analogue,[23] reaction of RuMeCN(CO)$_2$(PMe$_3$)$_2$ (**17**) with carbon monoxide resulted in the formation only of the cis acetyl product Ru(COMe)CN(CO)$_2$(PMe$_3$)$_2$ (**19**). All labeling studies of this system were therefore carried at room temperature in methylene chloride.

It was found that **17** reacts with ^{13}CO to give only Ru(COMe)CN(CO)(^{13}CO)(PMe$_3$)$_2$ (**20**), with none of the isotopomer **21** being observed in the ^{13}CO NMR spectrum. In addition, RuMeCN(^{13}CO)$_2$(PMe$_3$)$_2$ (**18**) reacts with normal CO to give only Ru(^{13}COMe)CN(CO)(^{13}CO)(PMe$_3$)$_2$ (**24**) and with ^{13}CO to give the triply labeled product Ru(^{13}COMe)CN(^{13}CO)$_2$(PMe$_3$)$_2$ (**25**). Neither incorporation of the incoming CO into the acetyl group nor the presence of the other isotopomer was observed in either case, and thus these reactions also appear to proceed cleanly as in Scheme II rather than as in Scheme III.

Although we have shown the five-coordinated intermediates in Scheme II as square-pyramidal rather than trigonal-pyramidal, differing opinions and suggestions concerning the structures of these types of complexes have been offered previously.[14,15,21] We also note that there is probably a subtle balance between the two types of d^6 structures.[24] However, recent X-ray crystal structure determinations of similar ruthenium and osmium compounds of the type MRCl(CO)L$_2$ (M = Ru, Os; R = H,[25] CH=CHPh,[25] *p*-tolyl[26]) demonstrate an apparent proclivity for square-pyramidal structures for this series of compounds, and the same is presumably true also for the compounds discussed here.

Summary

Compounds of the type MMeX(CO)$_2$(PMe$_3$)$_2$ (M = Fe, Ru; X = I, CN) react with ^{13}CO in a variety of solvents to give the products of the same basic stereochemistry, i.e.



Two mechanisms are involved, depending essentially on the ease of substitution of the anion, X, by carbon monoxide. Thus carbonylation of the iodoiron compound FeMeI(CO)$_2$(PMe$_3$)$_2$ in the relatively polar solvent methylene chloride proceeds via an ionic intermediate as in Scheme III. In contrast, carbonylation of the same compound in the less polar solvents *n*-hexane and toluene, in which the ionic species is apparently not stabilized, proceeds via nonionic intermediates as in Scheme II.

In contrast, carbonylation reactions of the cyanoiron compound FeMeCN(CO)$_2$(PMe$_3$)$_2$, in which the anion is a poorer leaving group, and of the ruthenium compounds RuMeX(CO)$_2$(PMe$_3$)$_2$ (X = I, CN), in which the metal–anion bond strengths are probably higher, also proceed via the mechanism illustrated in Scheme II rather than via anion substitution, even in methylene chloride.

In all cases, the step involving formation of the acetyl group involves formal methyl rather than formal carbon monoxide migration.

Acknowledgment. This research was supported by the Italian National Research Council (CNR, Programma Finalizzato Chimica Fine e Secondaria) and the Natural Sciences and Engineering Research Council of Canada.

Registry No. **1**, 33542-07-3; **2**, 88003-85-4; **3**, 116697-45-1; **4**, 88081-61-2; **5**, 116697-46-2; **6**, 88228-54-0; **7**, 116697-47-3; **8**, 88003-88-7; **9**, 116635-39-3; **10**, 116635-40-6; **11**, 94249-45-3; **12**, 116635-42-8; **13**, 88003-89-8; **14**, 116635-43-9; **16**, 116635-44-0; **17**, 116635-45-1; **18**, 116635-46-2; **19**, 116635-47-3; **20**, 116635-48-4; **22**, 116635-49-5; **24**, 116635-51-9; **25**, 116635-52-0; ^{13}CO, 1641-69-6; *trans*-Fe(^{13}COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$, 91083-45-3; *trans*-Ru(COMe)I(CO)$_2$(PMe$_3$)$_2$, 88080-77-7; *trans*-Ru(^{13}COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$, 116697-48-4; *trans*-Ru(COMe)I(^{13}CO)$_2$(PMe$_3$)$_2$, 116635-50-8.

---

(23) Reichenbach, G.; Cardaci, G.; Bellachioma, G. *J. Chem. Soc., Dalton Trans.* **1982**, 847.

(24) Hoffmann, R.; Rossi, A. R. *Inorg. Chem.* **1975**, *14*, 365.

(25) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(26) Rober, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1.