

# Oxygen Atom Transfer Reactions to Metal Carbonyls. Kinetics and Mechanism of CO Substitution of $M(\text{CO})_5$ ( $M = \text{Fe, Ru, Os}$ ) in the Presence of $(\text{CH}_3)_3\text{NO}$

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Reported are rates of reaction and activation parameters for CO substitution by  $\text{PPh}_3$  of  $M(\text{CO})_5$  ( $M = \text{Fe, Ru, Os}$ ) in the presence of  $(\text{CH}_3)_3\text{NO}$ . The reactions follow a second-order rate law, being first-order in concentrations of  $M(\text{CO})_5$  and of  $(\text{CH}_3)_3\text{NO}$  but zero-order in  $\text{PPh}_3$  concentration. The reaction rates show an approximate overall fourfold increase in the order  $\text{Fe} < \text{Ru} \lesssim \text{Os}$ . This contrasts the roughly 40-fold decrease in rate in the order  $\text{Fe} > \text{Ru} > \text{Os}$  for  $M_3(\text{CO})_{12}$ . An attempt is made to account for the relative reaction rates of the  $M(\text{CO})_5$  compounds and for why the order differs from that of the corresponding metal carbonyl clusters.

## Introduction

The late Walter Hieber,<sup>1</sup> sometimes referred to as the "father of metal carbonyl chemistry", was, in 1959, the first to report an oxygen atom transfer to metal carbonyls. Alper and Edward<sup>2</sup> reported the generality of this reaction and suggested a mechanism. Shvo and Hazum<sup>3</sup> in 1975 made use of the reaction at room temperature between  $\text{Fe}(\text{CO})_5$  and various dienes, in the presence of  $(\text{CH}_3)_3\text{NO}$ , to prepare  $\text{Fe}(\text{CO})_3(\text{dienes})$  in good yields. Since that time the reaction has often been used for the synthesis of metal carbonyl derivatives.<sup>4</sup>

Almost 3 decades after the Hieber discovery and the extensive use of these reactions, the kinetics and mechanism of CO substitutions of  $M(\text{CO})_6$  ( $M = \text{Cr, Mo, W}$ ) in the presence of  $(\text{CH}_3)_3\text{NO}$  were reported.<sup>5</sup> The mechanism appears to be that proposed earlier<sup>2</sup> of a nucleophilic attack of the amine oxide on a carbonyl carbon to form the good leaving group  $\text{CO}_2$  and a coordinatively unsaturated metal carbonyl which then readily reacts with the entering nucleophile. The rates of reaction showed that the rates increase slightly in the order  $\text{Cr} < \text{Mo} < \text{W}$ , whereas CO substitution reactions in absence of  $(\text{CH}_3)_3\text{NO}$  are in accord with the usually greater substitution lability of the second-row transition-metal organometallic compounds.<sup>6</sup>

Reactions of  $M_3(\text{CO})_{12}$  ( $M = \text{Fe, Ru, Os}$ ) are exceptions to the usual "rule" of the second-row transition-metal complexes being the fastest to react for a given triad of organometallic compounds. The rates of CO substitution of these metal carbonyl clusters decrease in the order  $\text{Fe} > \text{Ru} > \text{Os}$ , both for the reaction in absence<sup>7</sup> of and in presence<sup>8</sup> of  $(\text{CH}_3)_3\text{NO}$ . It is the latter case which this paper addresses. The suggestion was made that the order of reactivity of  $M_3(\text{CO})_{12}$  with  $(\text{CH}_3)_3\text{NO}$  decreases with decreasing tendency of bridging CO,  $M-\text{C}(=\text{O})-M$ , formation in the transition state for reaction. Since bridging COs are believed to be more electron withdrawing than are terminal COs,<sup>9</sup> the formation of bridging COs in the transition state should better accommodate the developing negative charge in the transition state due to nucleophilic attack. This attack is on a terminal CO, which forms  $\text{CO}_2$  and leaves to open a coordination site on the metal. In order to examine further the importance of this CO bridging concept for the reactivities of these iron triad

clusters, it was decided to investigate the monomeric carbonyls  $M(\text{CO})_5$  ( $M = \text{Fe, Ru, Os}$ ) where bridging COs cannot be a factor. This paper reports the results of a kinetic study on replacement of CO by  $\text{PPh}_3$  for the carbonyls  $M(\text{CO})_5$  in the presence of  $(\text{CH}_3)_3\text{NO}$ .

## Experimental Section

**Chemical Compounds.**  $\text{Fe}(\text{CO})_5$  was obtained from Aldrich Chemical Co. and purified by distillation under reduced pressure.  $\text{Ru}(\text{CO})_5$  was prepared by photolysis of  $\text{Ru}_3(\text{CO})_{12}$ <sup>10</sup> which was obtained from Aldrich Chemical Co. Saturated ( $\sim 10^{-3}$  M) and degassed solutions of  $\text{Ru}_3(\text{CO})_{12}$  in hexane were irradiated under an atmosphere of CO in bright sunlight or with a UV lamp. The reaction was followed by monitoring the IR spectrum of the solution. The initial IR bands of  $\text{Ru}_3(\text{CO})_{12}$  at 2065, 2035, and 2012  $\text{cm}^{-1}$  disappeared, and bands at 2037 (s) and 1998 (vs)  $\text{cm}^{-1}$  appeared due to the formation of  $\text{Ru}(\text{CO})_5$ .<sup>11</sup>  $\text{Os}(\text{CO})_5$  was provided by Professor Josef Takats and Dr. Gong-Yu Kiel.  $\text{PPh}_3$  was purified by recrystallization from anhydrous alcohol.  $(\text{C}_6\text{H}_5)_3\text{NO} \cdot 2\text{H}_2\text{O}$  was obtained from Aldrich Chemical Co. and was dehydrated by sublimation before use. Alcohol and hexane were dehydrated with  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  and Na, respectively, and distilled under  $\text{N}_2$  atmosphere before use.

**Kinetic Study.** All the reactions were followed with a Nicolet 7199 FT-IR spectrophotometer using a special P/N 20.500 variable-temperature IR cell with 0.5-mm AgCl windows. Constant temperature was maintained by immersing a hollow copper coil into the solvent chamber of the variable-temperature IR cell. The water from the constant temperature bath (Neslab RTE-8) circulated through the copper coil, and the temperature of the cell was determined from a copper thermocouple attached to the interior of the cell. All of the reactions were carried out in 1/2 (v/v)  $\text{C}_2\text{H}_5\text{OH}/n\text{-C}_6\text{H}_{14}$  mixed solvent and at conditions where the concentration of  $(\text{CH}_3)_3\text{NO}$  and of  $\text{PPh}_3$  are at least 10 times greater than that of  $M(\text{CO})_5$ . In a typical experiment, a solution of  $(\text{CH}_3)_3\text{NO}$  in  $\text{C}_2\text{H}_5\text{OH}$  and a solution of  $\text{PPh}_3$  in hexane were

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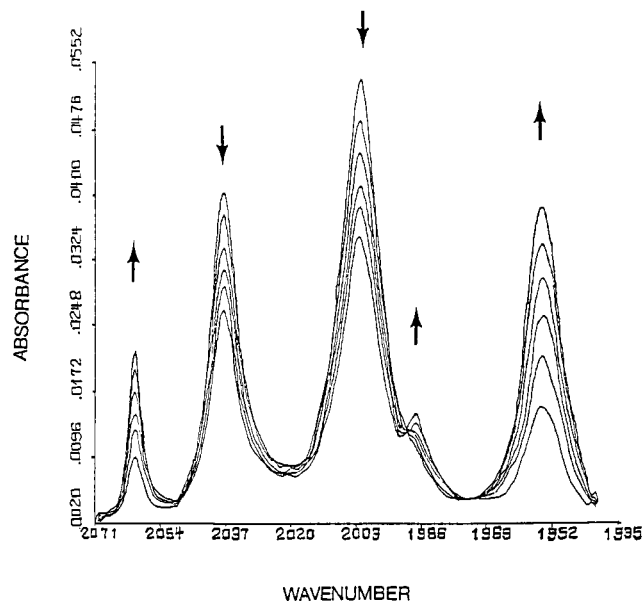


Figure 1. Infrared  $\nu_{\text{CO}}$  absorbance changes vs time for the reaction (eq 2) ( $M = \text{Ru}$ ) at room temperature.

Table I. Observed Rate Constants for the Reaction (Eq 2) of  $\text{M}(\text{CO})_5$  with  $\text{PPh}_3$  in the Presence of  $(\text{CH}_3)_3\text{NO}$  in 1/2 (v/v)  $\text{C}_2\text{H}_5\text{OH}-n\text{-C}_6\text{H}_{14}$  Solution

M	$10^3[\text{PPh}_3], \text{M}$	$10^4 k_{\text{obsd}}, \text{s}^{-1}$
Fe <sup>a</sup>	4.47	6.73
	8.94	6.98
	13.4	6.35
	17.88	7.57
Ru <sup>b</sup>	2.52	6.78
	5.05	8.36
	7.57	7.19
Os <sup>c</sup>	3.20	17.1
	6.40	16.2
	9.60	17.5

<sup>a</sup>  $t = 29.2^\circ\text{C}$ .  $[(\text{CH}_3)_3\text{NO}] = 12.5 \times 10^{-3} \text{M}$ . <sup>b</sup>  $t = 34.0^\circ\text{C}$ .  $[(\text{C}_2\text{H}_5)_3\text{NO}] = 2.47 \times 10^{-3} \text{M}$ . <sup>c</sup>  $t = 34.5^\circ\text{C}$ .  $[(\text{CH}_3)_3\text{NO}] = 7.28 \times 10^{-3} \text{M}$ .

synged into the flask in appropriate volumes, and then a solution of  $\text{Fe}(\text{CO})_5$  in hexane was synged into the flask. After the flask was vigorously shaken, an aliquot was removed by syringe, and the aliquot was synged into an IR cell flushed with  $\text{N}_2$  and sealed with a rubber septa. After a few minutes of temperature equilibration, the resultant spectral changes were monitored. Rate data were obtained by following the disappearance of CO stretching bands of  $\text{M}(\text{CO})_5$  and using eq 1 for calculation. Plots of  $-\ln A_t$  vs time were linear over 2 half-lives (linear correlation coefficient  $> 0.995$ ).

$$\ln A_t = -k_{\text{obsd}}t + \text{constant} \quad (1)$$

## Results

The rates of reaction (eq 2) were monitored by following changes in the IR absorption spectra with time. Spectral  $\text{M}(\text{CO})_5 + (\text{CH}_3)_3\text{NO} + \text{PPh}_3 \rightarrow \text{M}(\text{CO})_4\text{PPh}_3 + \text{CO}_2 + (\text{CH}_3)_3\text{N}$  (2)

changes (Figure 1) suggest a good stoichiometric reaction, affording monosubstituted products. In all cases, the reaction products had IR spectra in agreement with reported<sup>12</sup> spectra of known compounds.

Plots of  $-\ln A_t$  vs time for reaction (eq 2) were linear over 2 half-lives. The slopes of these lines gave  $k_{\text{obsd}}$ . Plots of

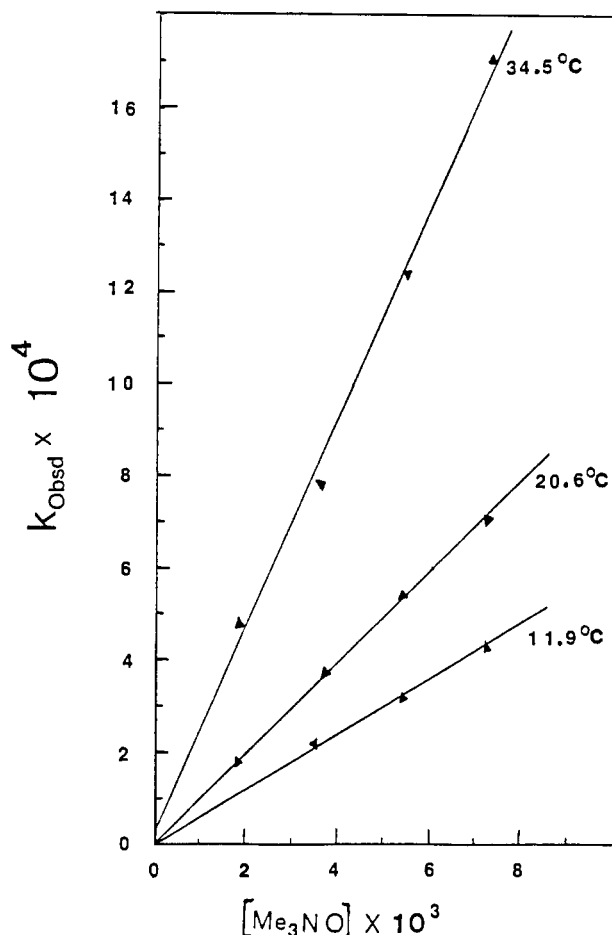


Figure 2. Plot of  $k_{\text{obsd}}$  vs  $(\text{CH}_3)_3\text{NO}$  concentration for the reaction (eq 2) ( $M = \text{Os}$ ).

Table II. Second-Order Rate Constants and Activation Parameters for Reaction (Eq 2)

M	$t, ^\circ\text{C}$	$k_2, \text{M}^{-1}\cdot\text{s}^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{cal/(K}\cdot\text{mol)}$
Fe	11.3	$1.02 \times 10^{-2}$		
	20.6	$2.37 \times 10^{-2}$	$14.5 \pm 0.2$ ( $12.5 \pm 0.6$ ) <sup>a</sup>	$-16.5 \pm 0.03$ ( $-14.0 \pm 2.1$ ) <sup>a</sup>
Ru	29.2	$5.10 \times 10^{-2}$		
	33.9	$7.21 \times 10^{-2}$		
	15.9	$5.54 \times 10^{-2}$		
	20.6	$7.41 \times 10^{-2}$	$13.8 \pm 0.9$ ( $12.1 \pm 0.2$ ) <sup>a</sup>	$-16.6 \pm 0.09$ ( $-18.4 \pm 0.5$ ) <sup>a</sup>
Os	28.1	$15.3 \times 10^{-2}$		
	34.0	$23.1 \times 10^{-2}$		
	11.9	$5.60 \times 10^{-2}$		
	20.6	$9.70 \times 10^{-2}$	$10.3 \pm 0.2$ ( $17.1 \pm 0.3$ ) <sup>a</sup>	$-28.3 \pm 0.03$ ( $-5.9 \pm 1.0$ ) <sup>a</sup>
	34.5	$22.8 \times 10^{-2}$		

<sup>a</sup> Activation parameters in parentheses are for the reactions of  $\text{M}_3(\text{CO})_{12}$  ( $M = \text{Fe, Ru, Os}$ ) from ref 8.

$k_{\text{obsd}}$  vs  $[(\text{CH}_3)_3\text{NO}]$  show a first-order dependence on the concentration of  $(\text{CH}_3)_3\text{NO}$  (Figure 2). Reaction rates were independent of the  $\text{PPh}_3$  concentration (Table I). Thus, the reactions obey a second-order rate law given by eq 3. Second-order rate constants and activation parameters for the reaction (eq 2) are included in Table II.

$$-d[\text{M}(\text{CO})_5]/dt = k_2[\text{M}(\text{CO})_5][(\text{CH}_3)_3\text{NO}] \quad (3)$$

## Discussion

The reactions of  $\text{M}(\text{CO})_5$  ( $M = \text{Fe, Ru, Os}$ ) with  $\text{PPh}_3$  in the presence of  $(\text{CH}_3)_3\text{NO}$  afford the monosubstituted complexes  $\text{M}(\text{CO})_4\text{PPh}_3$  (eq 2). The rates of disappearance of  $\text{M}(\text{CO})_5$  follow a second-order rate law (eq 3), first order

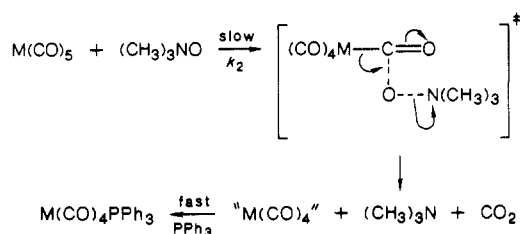
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**Table III. Second-Order Rate Constants for Reaction (Eq 2) and Values of CO Stretching Frequencies,  $\nu_{\text{CO}}$ , for  $\text{M}(\text{CO})_5$** 

compd	$\nu_{\text{CO}}$ , <sup>a</sup> $\text{cm}^{-1}$	$k_2$ , <sup>b</sup> $\text{M}^{-1} \text{s}^{-1}$
$\text{Fe}(\text{CO})_5$	2022.5	$2.37 \times 10^{-2}$
	2000.5	
$\text{Ru}(\text{CO})_5$	2036.5	$7.41 \times 10^{-2}$
	2001.5	
$\text{Os}(\text{CO})_5$	2035.0	$9.70 \times 10^{-2}$
	1993.0	

<sup>a</sup>Reference 12. <sup>b</sup>At 20.6 °C. The rate constants<sup>8</sup> of  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Ru}_3(\text{CO})_{12}$ , and  $\text{Os}_3(\text{CO})_{12}$  are 2.78, 0.568, and 0.0608, respectively, at the same temperature in  $\text{CHCl}_3/\text{C}_2\text{H}_5\text{OH}$  (v/v, 2/1); and the rate constants determined in this study for the clusters in the same solvent, 1/2 (v/v)  $\text{C}_2\text{H}_5\text{OH}/n\text{-C}_6\text{H}_{14}$ , are 13.2 (estimated), 3.05, and 0.256, respectively.

in  $\text{M}(\text{CO})_5$  and in  $(\text{CH}_3)_3\text{NO}$  concentrations but zero-order in  $\text{PPh}_3$  concentration (Table I). This rate law and kinetic behavior is the same as that reported earlier for the corresponding reactions of  $\text{M}(\text{CO})_6$ <sup>5</sup> and of  $\text{M}_3(\text{CO})_{12}$ .<sup>8</sup> Accordingly, the same mechanism is proposed.



This associative mechanism is further supported by the activation parameters for the reactions, which are low values of  $\Delta H^\ddagger$  and negative values of  $\Delta S^\ddagger$  (Table II).

The reactions (eq 2) were carried out in 1/2 (v/v)  $\text{C}_2\text{H}_5\text{OH}/n\text{-C}_6\text{H}_{14}$  mixed solvent because of the small solubility of  $(\text{CH}_3)_3\text{NO}$  in  $n\text{-C}_6\text{H}_{14}$ . In other aprotic solvents of higher dielectric strength (tetrahydrofuran) in which  $(\text{CH}_3)_3\text{NO}$  can be dissolved, the reactions are too fast to be followed by conventional spectroscopy. Although quantitative comparisons of relative activities is impossible between  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and  $\text{M}(\text{CO})_5$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ), what is known is that the  $\text{M}(\text{CO})_6$  compounds do not react with  $(\text{CH}_3)_3\text{NO}$  under our experimental condition even after 1 day at room temperature. Such a large difference between the reactivities of  $\text{M}(\text{CO})_6$  and  $\text{M}(\text{CO})_5$  towards  $(\text{CH}_3)_3\text{NO}$  is in agreement with previous studies<sup>13</sup> which show that rates of nucleophilic attack on carbon in metal carbonyls increase with increasing CO stretching frequencies. The values of  $\nu_{\text{CO}}$  for  $\text{M}(\text{CO})_6$  are near 1980  $\text{cm}^{-1}$ , compared with values of about 2030  $\text{cm}^{-1}$  for  $\text{M}(\text{CO})_5$  (Table III). One of the reviewers suggests that steric effects may retard nucleophilic attack at  $\text{M}(\text{CO})_6$ , causing it to react slower than  $\text{M}(\text{CO})_5$ . Although this is a reasonable suggestion, it is known<sup>14</sup> that the  $\text{M}(\text{CO})_5\text{L}$  compounds do not decrease in rates of reaction with increasing cone angle of L.

In order to compare rates of reaction of the  $\text{M}(\text{CO})_5$  carbonyls with the previously reported<sup>8</sup> rates for  $\text{M}_3(\text{CO})_{12}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ), it would have been necessary to use the solvent  $\text{CHCl}_3\text{-C}_2\text{H}_5\text{OH}$  which was used in the cluster study. Unfortunately, the reaction mixture for  $\text{Fe}(\text{CO})_5$  (eq 2) in this solvent becomes cloudy and gives spurious results. The reason for this is not known, but it may have to do with a reaction of the presumed active intermediate

$\text{Fe}(\text{CO})_4$  with  $\text{CHCl}_3$ .<sup>15</sup> For this reason, it was necessary to determine the rates of reaction of  $\text{M}_3(\text{CO})_{12}$  in  $\text{C}_2\text{H}_5\text{OH}/n\text{-C}_6\text{H}_{14}$  (Table III) in order to have a direct comparison with the rates of reaction of  $\text{M}(\text{CO})_5$  reported here.

The results show that for a given metal, except for osmium, the rates of reaction for  $\text{M}_3(\text{CO})_{12}$  are faster than for  $\text{M}(\text{CO})_5$ . For iron the rate difference is about 2 orders of magnitude, whereas it is approximately 1 order of magnitude for ruthenium, and  $\text{Os}_3(\text{CO})_{12}$  reacts at about the same rate as does  $\text{Os}(\text{CO})_5$ . This result is expected on the basis of the usual behavior that rates of nucleophilic attack on carbon of metal carbonyls increase with increasing frequencies of C-O stretch.<sup>13</sup> The highest values of  $\nu_{\text{CO}}$  for  $\text{M}_3(\text{CO})_{12}$  are approximately 2055  $\text{cm}^{-1}$ , compared with 2030  $\text{cm}^{-1}$  for  $\text{M}(\text{CO})_5$ .

That the largest rate difference between  $\text{M}(\text{CO})_5$  and  $\text{M}_3(\text{CO})_{12}$  is for iron and the smallest is for osmium can be rationalized in terms of formation of bridging carbonyls in the transition state for reaction of the metal carbonyl clusters.<sup>8,16</sup> Since it is known<sup>17</sup> that the degree of difficulty in forming bridging COs in  $\text{M}_3(\text{CO})_{12}$  clusters increases in the order  $\text{Fe} < \text{Ru} < \text{Os}$ , it follows that osmium would experience the greatest rate retardation. This then might explain why the osmium cluster reacts at about the same rate as does  $\text{Os}(\text{CO})_5$ , whereas the largest difference in rate is for iron which has bridging COs in the cluster ground state, and ruthenium experiences an intermediate difference between that of iron and of osmium. Although the CO bridging concept in assisting to dissipate negative charge<sup>9</sup> brought to the transition state by nucleophilic attack is perhaps attractive, surely other factors affect differences in rate between corresponding monomeric and cluster metal carbonyls. Steric effects, symmetry requirements, coordination number, and other factors can contribute to the stability of transition states for reactions.

Finally, the reactivities of  $\text{M}(\text{CO})_5$  with  $(\text{CH}_3)_3\text{NO}$  increase in the order  $\text{Fe} < \text{Ru} < \text{Os}$  (Table III). This is in agreement with the general correlation<sup>13</sup> between increasing rates of nucleophilic attack on carbon in metal carbonyls with increasing values of  $\nu_{\text{CO}}$ . The rate order is opposite to what was observed for similar reactions of  $\text{M}_3(\text{CO})_{12}$ , where the rates decrease in the order  $\text{Fe} > \text{Ru} > \text{Os}$ . The same order of reactivities was obtained<sup>16</sup> for the reaction of  $\text{M}(\text{CO})_5$  and of  $\text{M}_3(\text{CO})_{12}$  with  $\text{CH}_3\text{O}^-$  to form corresponding methoxy carbonyl adducts. This order for the cluster is attributed<sup>8,16</sup> to the increasing difficulty in forming bridging COs in the transition state for reaction. It is further noteworthy that the mononuclear metal carbonyls  $\text{M}(\text{CO})_5$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) and  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ),<sup>5</sup> respectively, have a similar order of reactivity with  $(\text{CH}_3)_3\text{NO}$ . Furthermore, for each triad the difference in rate is small (4 times for the Fe triad and 2.5 times for the Cr triad), suggesting the metal plays an indirect role in these reactions where attack is on the carbonyl carbon. In contrast to these small differences, there are large differences<sup>10,18</sup> for rates of thermal CO substitution in the absence of  $(\text{CH}_3)_3\text{NO}$  for each of the triads.

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**Registry No.** Fe(CO)<sub>5</sub>, 13463-40-6; Ru(CO)<sub>5</sub>, 16406-48-7; Os(CO)<sub>5</sub>, 16406-49-8; PPh<sub>3</sub>, 603-35-0; (CH<sub>3</sub>)<sub>3</sub>NO, 1184-78-7.

**Supplementary Material Available:** Additional values are given of *k*<sub>obsd</sub> for reactions (eq 2) at different concentrations of (CH<sub>3</sub>)<sub>3</sub>NO and different temperatures (Table S1) (2 pages). Ordering information is given on any current masthead page.

## New Approaches to Heteroatomic Chelation of Early and Late Transition Metals. Synthesis and Characterization of Cyclometallaphosphoranimine- and Cyclometallaphosphoraniminatophosphanes (and Arsanes) of Mo(0), W(0), Rh(I), and Ir(I) Derived from Novel Heterodifunctional Phosphorus and Arsenic Ligands

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Oxidation of one phosphorus in Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> and in Ph<sub>2</sub>PC<sub>2</sub>H<sub>4</sub>AsPh<sub>2</sub> with Me<sub>3</sub>SiN<sub>3</sub> gives new heterodifunctional ligands with phosphorus(III) (or arsenic(III)) and nitrogen base centers. Chelate complexes LL'M(CO)<sub>4</sub> (M = Mo, W), formed by Me<sub>3</sub>SiN=PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (1, LL'), have been fully characterized by <sup>31</sup>P, <sup>29</sup>Si, and <sup>1</sup>H NMR and IR spectroscopy. 1 reacts with activated fluoroaromatics (pentafluoropyridine and pentafluorobenzonitrile) eliminating Me<sub>3</sub>SiF to give quantitative yields of the compounds XN=PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (5, X = *p*-C<sub>6</sub>F<sub>4</sub>CN; 6, X = *p*-C<sub>6</sub>F<sub>4</sub>N) wherein the N atom of the ligand bears a fluoroaromatic substituent. Exclusive substitution via the para position of the fluoroaromatic ring occurs. [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> reacts with 1, 5, and 6 to form the corresponding monomeric chelate complexes with both P and N coordinated to Rh(I). These complexes (14, 7, 8) show characteristic <sup>1</sup>J<sub>PRh</sub> values of 160–170 Hz indicating direct Rh–P(III) binding. Smaller coupling with the remote P(V) atom is also observable. The CO is cis to the P(III) center. The N-silylated As/P derivative Me<sub>3</sub>SiN=PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub> (9) also forms the chelated LL'/Rh(CO)Cl complex (10) which behaves very similarly to the complex derived from 1. *ν*<sub>PN</sub> values for the coordinated iminato phosphorane unit (1120–1125 cm<sup>-1</sup> in Mo(0) and W(0) complexes 2 and 3 and 1142 cm<sup>-1</sup> for N-silylated complexes of Rh from 1 and 9 (14 and 10)) shift to significantly lower values in the fluorocarbon chelates (7, 8) (1080 cm<sup>-1</sup>) as the result of the significant reduction in electron density at the nitrogen. [M(cod)Cl]<sub>2</sub> (M = Rh, Ir) complexes eliminate Me<sub>3</sub>SiCl in reactions with 1 and 9 to form the metallacycles N=PPh<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>EPh<sub>2</sub>M(cod) (4, M = Ir, E = P, n = 1; 13, M = Rh, E = P, n = 1; 11, M = Rh, E = As, n = 2; 12, M = Ir, E = As, n = 2). These monomeric compounds that contain a metal–nitrogen σ bond and a coordinated P or As atom are characterized by a marked low-field <sup>31</sup>P NMR shift of the P(V) center suggesting substantial delocalization in the P=N–M portion of the molecule. The *ν*<sub>PN</sub> characteristic value for these complexes (4, 13, 11, 12) is approximately 1230 cm<sup>-1</sup>. These latter compounds provide a new class of nitrogen-bonded metallacycles of the late transition metals.

### Introduction

Whereas a large class of homoatomic chelated and bridged transition-metal complexes based on the alkane diphosphanes R<sub>2</sub>P(CR'<sub>2</sub>)<sub>n</sub>PR<sub>2</sub> are known,<sup>1–4</sup> extension of these frameworks by introducing an additional heteroatomic donor site (e.g., partial oxidation) to achieve systems of heteroatomic bridged complexes is limited. This is in part due to the difficulties involved in the chemical mod-

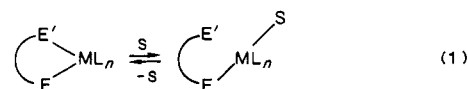
ifications of the ligands themselves to create heteroatomic reactive sites,<sup>5</sup> sites which will be particularly suitable for binding the metals of interest. Heterodifunctional ligands also provide contrasting binding properties for metals, and thus effective catalysts may be generated from complexes of bifunctional chelate ligands in which one substituent is more loosely bound than the other so that an equilibrium providing access to a reactive intermediate can be established.

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