the addition of Cl^- (in the form of benzyltriethylammonium chloride) to electrochemically and chemically generated solutions of the cationic molybdenum tricarbonyls $[(\eta^3\text{-all})Mo(CO)_3(L\text{-}L)]^+$ that contain the dppm and dppe ligands resulted in the formation of an equilibrium between the catonic tricarbonyl species and the neutral precursor dicarbonyl complexes $(\eta^3\text{-all})MoCl(CO)_2(L\text{-}L)$. A similar equilibrium, which was confirmed by IR spectroscopy (with the OTTLE) and cyclic voltammetry, was established upon treating the chemically prepared tricarbonyl cation $[(\eta^3\text{-all})W(CO)_3(dppe)]^+$ with Cl^-. However, the electrochemically generated tricarbonyl complex of tungsten, which we believe is $(\eta^1\text{-all})WCl(CO)_3(dppe)$, was unaffected by Cl^-, indicating that this species and presumably the dpae analogue XI are structurally different from the other systems.

In an effort to elucidate the mechanism for the formation of the molybdenum tricarbonyl cations $[(\eta^3\text{-all})Mo(CO)_3(L\text{-}L)]^+$ (for L-L = dppm or dppe) from the electrochemically generated monocations $[(\eta^3\text{-all})MoCl(CO)_2(L\text{-}L)]^+$, the effect of an excess of CO(g) upon the redox chemistry was studied. The bulk electrolysis (at +0.75 V) of solutions that had been saturated with CO(g) produced the cation $[(\eta^3\text{-all})MoCl(CO)_2(L\text{-}L)]^+$ with $n_{app} \approx 1$ without any perceptible decomposition. Decomposition to the tricarbonyl is then initiated by the *removal* of CO(g). IR spectroscopy of these quickly decomposing solutions ($t_{1/2} \approx 1$ min) showed that the tricarbonyl $[(\eta^3\text{-all})Mo(CO)_3(L\text{-}L)]^+$ was the only carbonyl-containing product.

The preceding observations can be incorporated into a plausible mechanism (eq 1-4). In these reactions, braces denote a very

$$(\eta^3\text{-all})MoX(CO)_2(L\text{-}L \rightarrow [(\eta^3\text{-all})MoX(CO)_2(L\text{-}L)]^+ + e^- \quad (1)$$

$$[(\eta^3\text{-all})MoX(CO)_2(L\text{-}L)]^+ \rightarrow \{[(\eta^3\text{-all})MoX(CO)(L\text{-}L)]^+\} + CO \quad (2)$$

$$[(\eta^3\text{-all})MoX(CO)_2(L\text{-}L)]^+ + \{[(\eta^3\text{-all})MoX(CO)(L\text{-}L)]^+\} \rightarrow [(\eta^3\text{-all})Mo(CO)_3(L\text{-}L)]^+ + \{[(\eta^3\text{-all})MoX_2(L\text{-}L)]^+\} \quad (3)$$

$$\{[(\eta^3\text{-all})MoX_2(L\text{-}L)]^+\} + CO \rightarrow \{[(\eta^3\text{-all})MoX_2(CO)(L\text{-}L)]^+\} \rightarrow \text{oxidation and decomposition} \quad (4)$$

unstable species. Since the monocation produced by oxidation of the neutral species (eq 1) is stabilized in the presence of added CO(g), the first chemical step is probably the loss of a carbonyl ligand (eq 2). There is no evidence that the 17-electron cation $[(\eta^3\text{-all})MoX(CO)_2(L\text{-}L)]^+$ reacts with CO to form the tricarbonyl $[(\eta^3\text{-all})Mo(CO)_3(L\text{-}L)]^{2+}$. Note that the relative instability of this later dication has been demonstrated (vide supra) by the irreversibility of the oxidation of $[(\eta^3\text{-all})Mo(CO)_3(L\text{-}L)]^+$ to $[(\eta^3\text{-all})Mo(CO)_3(L\text{-}L)]^{2+}$ (see Figure S2). Consequently, this dication would not be a stable chemical product formed by $[(\eta^3\text{-all})MoX(CO)_2(L\text{-}L)]^+$ in the presence of CO(g). Subsequent reaction of the highly reactive 15-electron monocarbonyl cation $[(\eta^3\text{-all})MoX(CO)(L\text{-}L)]^+$ with the 17-electron dicarbonyl monocation seems to be a feasible means of producing the observed monocationic tricarbonyl (eq 3). This reaction, which formally represents a disproportionation (i.e. 2Mo(III) → Mo(II) + Mo(IV)), is written as giving the 14-electron Mo(IV) complex as a second product. This is an attractive possibility in view of the observed formation of transients having C-O stretching modes at very high frequencies, 2191 and 2164 cm^{-1}. Such a Mo(IV) complex would most likely scavenge any free CO in the system to form a 16-electron monocarbonyl complex that contains halide (eq 4). The ESR activity of the electrolyzed solution and the >1 coulometric electron count (Table I) can then be attributed to the subsequent oxidation and decomposition of this highly unstable moiety.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE85-06702 to R.A.W. and Grant No. CHE85-13732 to M.J.W.) for generous research support. The FTIR spectrometer was acquired through a DOD University Instrumentation Award (to M.J.W.). We appreciate the experimental assistance of Dennis S. Corrigan in recording the FTIR spectra and Dr. K. A. Conner for some very helpful preliminary experiments.

Registry No. I, 12245-57-7; II, 110174-39-5; III, 110222-34-9; IV, 47462-49-7; V, 12091-83-7; VI, 12245-84-0; VII, 57811-37-7; VIII, 60214-54-2; IX, 62662-28-6; X, 33135-95-4; XI, 66615-65-4; XII, 62960-06-9; $[(\eta^3\text{-all})MoCl(CO)_2(bpy)]PF_6$, 110174-41-9; $[(\eta^3\text{-all})MoCl(CO)_2(phen)]PF_6$, 110174-43-1; $[(\eta^3\text{-all})Mo(O_2CCF_3)(CO)_2(bpy)]PF_6$, 110174-45-3; $[(\eta^3\text{-all})Mo(CO)_3(dppm)]^+$, 66518-78-3; $[(\eta^3\text{-all})Mo(CO)_3(dppe)]^+$, 66518-74-9; $[(\eta^3\text{-all})Mo(CO)_3(dpae)]^+$, 110174-46-4; $[(\eta^3\text{-all})W(CO)_3(dppe)]^+$, 66518-80-7.

Supplementary Material Available: Figures S1 and S2, showing the cyclic voltammograms of $(\eta^3\text{-all})MoCl(CO)_2(dppm)$ and $[(\eta^3\text{-all})Mo(CO)_3(dppm)]^+ClO_4^-$ (2 pages). Ordering information is given on any current masthead page.

---

(34) Wong, C. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100.

Contribution from the Department of Chemistry, The University of British Columbia,
Vancouver, British Columbia, Canada V6T 1Y6

Reduction of $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ (M = Mo, W) Dimers by PMe_3: Synthesis and Properties of the Novel Complexes $M(NO)(PMe_3)_4I$[1]

Nancy J. Christensen, Allen D. Hunter, Peter Legzdins,* and Luis Sânchez[2]

Received April 1, 1987

The diiodo dimers $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ (M = Mo, W) react with 10 equiv of PMe_3 to produce the new electron-rich nitrosyl complexes $M(NO)(PMe_3)_4I$, the other product being $[(C_5H_5)PMe_3]I$. It has been shown that the formation of the tetrakis(phosphine) complexes proceeds sequentially via the isolable intermediate species $(\eta^5\text{-}C_5H_5)M(NO)I_2(PMe_3)$ and $[(\eta^5\text{-}C_5H_5)M(NO)I(PMe_3)_2]I$. Treatment of the diiodo dimers with 4 equiv of PMe_3 in the presence of a reducing agent such as sodium amalgam affords excellent yields of the related complexes $(\eta^5\text{-}C_5H_5)M(NO)(PMe_3)_2$ (M = Mo, W), which also contain electron-rich transition-metal centers. The analytical and spectroscopic properties of all new complexes prepared are presented.

Introduction

Because of its relatively small cone angle and strong Lewis basicity, trimethylphosphine (PMe_3) often exhibits distinctive behavior during its reactions with organo transition-metal complexes.[3] Particularly interesting in this regard are the reactions of PMe_3 with cyclopentadienyl-containing compounds. Previous work by Casey and co-workers[4] has established the occurrence

---

(1) Organometallic Nitrosyl Chemistry. 31. Part 30: Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1986**, *108*, 3843.

(2) Present address: Departamento de Quimica Inorgânica, Facultad de Quimica, Universidad de Sevilla, Sevilla, Spain.

(3) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(4) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307 and references cited therein.

0020-1669/87/1326-3344$01.50/0 © 1987 American Chemical Society

of some or all of the sequential substitution reactions summarized in eq 1 for a variety of such compounds, e.g. M = $Re(CO)_3$,

$$(\eta^5\text{-}C_5H_5)M \xrightleftharpoons[-PMe_3]{+PMe_3} (\eta^3\text{-}C_5H_5)M(PMe_3) \xrightleftharpoons[-PMe_3]{+PMe_3} (\eta^1\text{-}C_5H_5)M(PMe_3)_2 \xrightleftharpoons[-PMe_3]{+PMe_3} [M(PMe_3)_3]^+C_5H_5^- \quad (1)$$

Re(CO)(NO)Me, $Re(PMe_3)(NO)(Me)$, $Mo(CO)_2(NO)$, $W(CO)_2(NO)$, etc. We now wish to report the first examples of another mode of reactivity involving these reactants, namely displacement of the cyclopentadienyl ligand with concomitant reduction of the organometallic reagent, i.e.

$$(\eta^5\text{-}C_5H_5)M^+ + 3PMe_3 \rightarrow M(PMe_3)_2 + [(C_5H_5)PMe_3]^+ \quad (2)$$

The specific examples of reactions 2 that we have observed involve the compounds having M = $Mo(NO)(PMe_3)_2I$ or $W(NO)(PMe_3)_2I$. These compounds, in turn, result from the treatment of $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ (M = Mo or W) dimers with trimethylphosphine. Since most of this latter chemistry has not been previously described, it is also included in this report for completeness.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions in a well-ventilated fume hood. General procedures routinely employed in these laboratories have been described in detail previously.[5] The iodo nitrosyl reagents, $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$[6] and $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$,[7] and PMe_3[8] were prepared by published procedures. Some ^1H and ^{31}P NMR spectra were collected on a Varian XL 300 NMR spectrometer.

Syntheses of $(\eta^5\text{-}C_5H_5)M(NO)I_2(PMe_3)$ (M = Mo, W). To a rapidly stirred, purple suspension of $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$ (2.00 g, 2.25 mmol) in CH_2Cl_2 (100 mL) (ν_{NO} 1677 cm^{-1}) at room temperature was added PMe_3 (0.45 mL, 4.5 mmol) dropwise. The purple solid was gradually consumed over 30 min, and the final reaction mixture consisted of a clear, red solution whose IR spectrum exhibited a ν_{NO} at 1665 cm^{-1}. This solution was passed through a Florisil (60–100 mesh) column (2 × 3 cm) supported on a medium-porosity frit. Dropwise addition of hexanes (20 mL) to the filtrate over 1 h induced the precipitation of a red crystalline solid. This precipitate was collected by filtration, washed with hexanes (3 × 25 mL), and dried in vacuo (5 × 10^{-3} mm) for 3 h at room temperature to obtain 1.50 g (65% yield) of $(\eta^5\text{-}C_5H_5)Mo(NO)I_2(PMe_3)$ as an analytically pure, brick red powder.

The tungsten analogue was obtained similarly as a red powder in 82% yield. The analytical, mass spectral, IR, and ^1H NMR data for these and the other new complexes synthesized during this work are collected in Table I.

Syntheses of $[(\eta^5\text{-}C_5H_5)M(NO)I(PMe_3)_2]I$ (M = Mo, W). To a red solution of $(\eta^5\text{-}C_5H_5)Mo(NO)I_2(PMe_3)$ (1.00 g, 1.92 mmol) in THF (90 mL) (ν_{NO} 1643 cm^{-1}) was added PMe_3 (0.20 mL, 2.0 mmol), and the mixture was stirred at room temperature for 2 h. The red solution gradually became pale orange, and a bright orange solid precipitated. The final solution exhibited no absorptions attributable to nitrosyl-containing products in its IR spectrum. The precipitate was collected by filtration, washed with hexanes (3 × 10 mL), and dried under vacuum to yield 1.00 g (87%) of $[(\eta^5\text{-}C_5H_5)Mo(NO)I(PMe_3)_2]I$ as a bright yellow powder.

The tungsten congener was obtained analogously as a yellow powder in 75% yield based on $(\eta^5\text{-}C_5H_5)W(NO)I_2(PMe_3)$.

Syntheses of $M(NO)(PMe_3)_4I$ (M = Mo, W). To a stirred yellow slush of $[(\eta^5\text{-}C_5H_5)Mo(NO)I(PMe_3)_2]I$ (1.70 g, 3.00 mmol) in CH_3CN (80 mL) at −45 °C was added PMe_3 (0.90 mL, 9.0 mmol). The mixture became orange immediately. The cooling bath was removed, and a yellow microcystalline solid began to precipitate after ~2 min. The reaction mixture was allowed to warm to room temperature, was stirred for 3 h, and was then taken to dryness in vacuo. The resulting solid was transferred to a Soxhlet extractor and was extracted with Et_2O (400 mL)

Table I. Analytical and Spectroscopic Data for the Complexes

complex	color	anal. data, %						low-resoln mass spectral data,^{a} M$^+$	IR (CH_2Cl_2)	^1H NMR data, δ		
		C		H		N						
		calcd	found	calcd	found	calcd	found	m/z^b	ν_{NO}, cm^{-1}		$\eta^5\text{-}C_5H_5$	PMe_3
$(\eta^5\text{-}C_5H_5)Mo(NO)I_2(PMe_3)$	red	18.45	18.78	2.69	2.85	2.69	2.50	447^c	1665	isomer A	5.90 (d, $^3J_{^1H-^{31}P}$ = 2.8 Hz)	1.84 (d, $^2J_{^1H-^{31}P}$ = 10.5 Hz)^d
										isomer B	5.92 (d, $^3J_{^1H-^{31}P}$ = 2.8 Hz)	1.88 (d, $^2J_{^1H-^{31}P}$ = 10.5 Hz)^d
$(\eta^5\text{-}C_5H_5)W(NO)I_2(PMe_3)$	red	15.71	15.56	2.29	2.31	2.29	2.19	533^c	1638		5.96 (d, $^3J_{^1H-^{31}P}$ = 2.6 Hz)	1.91 (d, $^2J_{^1H-^{31}P}$ = 10.6 Hz)^d
$[(\eta^5\text{-}C_5H_5)Mo(NO)I(PMe_3)_2]I$	yellow	22.11	22.37	3.85	3.77	2.35	2.30		1668		6.09 (d, $^3J_{^1H-^{31}P}$ = 2.09 Hz)	1.97 (m, N^f = 10.8 Hz)^e
$[(\eta^5\text{-}C_5H_5)W(NO)I(PMe_3)_2]I$	yellow	19.22	19.51	3.34	3.52	2.03	2.04		1645		6.91 (t, $^3J_{^1H-^{31}P}$ = 1.9 Hz)	2.07 (m, N^f = 10.3 Hz)^d
$Mo(NO)(PMe_3)_4I$	yellow	25.87	26.14	6.51	6.48	2.51	2.75	559	1539			1.45 (m)^g
$W(NO)(PMe_3)_4I$	yellow	22.33	22.34	5.58	5.54	2.17	2.27	643	1522			1.52 (br s)^h
$(\eta^5\text{-}C_5H_5)Mo(NO)(PMe_3)_2$	orange	38.49	38.37	6.70	6.61	4.08	4.11	345	1523		4.88 (t, $^3J_{^1H-^{31}P}$ = 0.92 Hz)	1.16 (m, N^f = 7.44 Hz)^h
$(\eta^5\text{-}C_5H_5)W(NO)(PMe_3)_2$	orange	30.62	30.40	5.33	5.30	3.24	3.25	431	1510		5.02 (t, $^3J_{^1H-^{31}P}$ = 1.5 Hz)	1.61 (m, N^f = 7.5 Hz)^g

[a] Probe temperatures 100–150 °C. [b] Assignments involve the most abundant naturally occurring isotopes in each species (i.e., ^{98}Mo and ^{184}W). [c] Attributable to $[M - PMe_3]^+$. [d] CD_2Cl_2. [e] CD_3NO_2. [f] $N = |J_{AX} + J_{AX'}|$. [g] $(CD_3)_2CO$. [h] C_6D_6.

---

(5) Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* **1985**, *4*, 1263.
(6) James, T. A.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2526.
(7) Legzdins, P.; Martin, D. T.; Nurse, C. R. *Inorg. Chem.* **1980**, *19*, 1560.
(8) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

for 4 days to obtain a yellow crystalline solid suspended in a yellow solution in the receiving flask. Removal of solvent from the Et_2O extracts under reduced pressure afforded 1.44 g (86% yield) of $Mo(NO)(PMe_3)_4I$ as an analytically pure, yellow crystalline solid [$^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 0 °C) δ −10.7].

The complex, $Mo(NO)(PMe_3)_4I$, could also be synthesized directly by treating $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$ with 10 equiv of PMe_3 in CH_3CN at −45 °C. Workup of the final reaction mixture in the manner described in the preceding paragraph produced the desired product in 72% yield. The analogous tungsten complex, $W(NO)(PMe_3)_4I$, was synthesized directly from $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ in a similar manner by adding the PMe_3 to an acetonitrile solution of the diiodide dimer at −45 °C and then stirring the reaction mixture at room temperature for 5 days. The usual workup afforded the product in 50% yield.

The Soxhlet apparatus from the original synthesis of $Mo(NO)(PMe_3)_4I$ (vide supra) was transferred to a second receiving flask charged with CH_2Cl_2 (350 mL), and extraction was continued for a further 18 h. This operation produced a white powder suspended in a pale brown solution in the receiving flask. The white solid was collected by filtration on a medium-porosity frit, washed with CH_2Cl_2 (2 × 20 mL), and recrystallized from EtOH (200 mL) to obtain 0.23 g (29% yield) of $[(C_5H_5)PMe_3]I$ as a white, hygroscopic, crystalline solid. Anal. Calcd for $C_8H_{14}PI$: C, 35.84; H, 5.23; I, 47.37. Found: C, 36.21; H, 5.39; I, 47.00. DCIMS (700 °C): m/z 141 ($C_8H_{14}P^+$) [$(M + 1)^+$ peak not observed].

Syntheses of $(\eta^5\text{-}C_5H_5)M(NO)(PMe_3)_2$ (M = Mo, W). These new complexes were synthesized from the appropriate $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ dimers in the manner previously described for the preparation of their $PMePh_2$ analogues.[9] Both $(\eta^5\text{-}C_5H_5)Mo(NO)(PMe_3)_2$ and $(\eta^5\text{-}C_5H_5)W(NO)(PMe_3)_2$ were isolated as orange, crystalline solids in yields of 88% and 80%, respectively. Their spectroscopic and analytical data are included in Table I for comparison with the other PMe_3-containing compounds prepared.

Results and Discussion

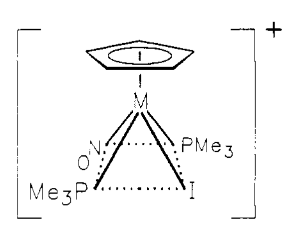
In the absence of an added reducing agent such as sodium amalgam, PMe_3 reacts with the $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ (M = Mo, W) dimers in a sequential manner. The first two steps of this sequence involve initial cleavage of the dimer, i.e.

$$[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2 + 2PMe_3 \rightarrow 2(\eta^5\text{-}C_5H_5)M(NO)I_2(PMe_3) \quad (3)$$

followed by displacement of one of the iodo ligands from the inner coordination sphere of the metal, i.e.

$$(\eta^5\text{-}C_5H_5)M(NO)I_2(PMe_3) + PMe_3 \rightarrow [(\eta^5\text{-}C_5H_5)M(NO)I(PMe_3)_2]I \quad (4)$$

The optimum conditions for effecting conversions 3 and 4 independently are presented in the Experimental Section, and the indicated products of both transformations are isolable in high yields as analytically pure solids. The brick red, neutral mono(phosphine) and yellow, cationic bis(phosphine) complexes exhibit spectroscopic properties similar to those described previously for their $PMePh_2$ analogues.[9,10] These properties (Table I) are consistent with their possessing "four-legged piano-stool" molecular structures. Interestingly, $(\eta^5\text{-}C_5H_5)Mo(NO)I_2(PMe_3)$ exists in CD_2Cl_2 as a mixture of isomers (arbitrarily designated as A and B) in a ratio of A:B ≃ 2:3 at ambient temperature. Presumably, one isomer has mutually cis iodo ligands, whereas in the other isomer these ligands are trans to one another. The congeneric tungsten complex, on the other hand, exists in CD_2Cl_2 exclusively as one isomer. Unfortunately, the $^3J_{H-^{31}P}$ values exhibited by the signals due to the cyclopentadienyl protons in all three cases are approximately the same (Table I), thereby precluding definite structural assignments to the individual isomers.[9] On the other hand, the ^1H and ^{31}P NMR data for both $[(\eta^5\text{-}C_5H_5)M(NO)I(PMe_3)_2]I$ (M = Mo, W) salts indicate that the cations exist in solutions as the single isomers having mutually trans PMe_3 ligands, i.e.

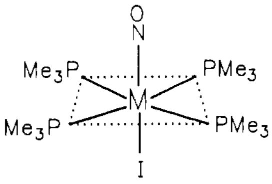


The final step in the sequential reactions of PMe_3 with the $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ dimers[11] involves the displacement of the cyclopentadienyl rings from the $[(\eta^5\text{-}C_5H_5)M(NO)I(PMe_3)_2]^+$ cations formed via conversions 4, i.e.

$$[(\eta^5\text{-}C_5H_5)M(NO)I(PMe_3)_2]I + 3PMe_3 \rightarrow M(NO)(PMe_3)_4I + [(C_5H_5)PMe_3]I \quad (5)$$

These transformations are particular examples of the generalized reaction represented by eq 2, the formal oxidation states of the transition metals decreasing by 2 units in going from reactant to product. Reactions 5 are most cleanly effected with CH_3CN as solvent, the conversion having M = Mo proceeding more rapidly to completion (3 h) than that having M = W (5 days). The new $M(NO)(PMe_3)_4I$ product complexes are isolable as yellow, diamagnetic solids in excellent yields. These solids are very air- and moisture-sensitive and decompose at room temperature in chlorinated organic solvents, particularly rapidly in $CHCl_3$ but more slowly in CH_2Cl_2. The very low nitrosyl-stretching frequencies evident in the IR spectra of these compounds (i.e. ν_{NO} (CH_2Cl_2) of 1539 and 1522 cm^{-1} for the molybdenum- and tungsten-containing species, respectively) indicate the presence of very electron-rich metal centers. Indeed, these frequencies are only slightly higher in energy than those exhibited by the related $(\eta^5\text{-}C_5H_5)M(NO)(PMe_3)_2$ compounds (vide infra).

The ^1H NMR spectra of the $M(NO)(PMe_3)_4I$ complexes (formal $AA'A''A'''X_9X'_9X''_9X'''_9$ spin systems) are quite simple in appearance. Furthermore, the $^{31}P\{^1H\}$ NMR spectrum of $Mo(NO)(PMe_3)_4I$ in $C_6D_5CD_3$ consists of a sharp singlet from +25 °C to −75 °C. Taken together, these spectroscopic properties are in accord with the tetrakis(phosphine) complexes possessing octahedral molecular structures with mutually trans iodo and nitrosyl ligands, i.e.



Analogous molecular structures have been previously proposed for the related compounds $Mo(NO)(dppe)_2Cl$,[12] $Mo(NO)(PPh_2H)_4Cl$,[12] and $M(NO)(CO)_4X$ (M = Mo, W; X = Cl, Br, I).[13]

The fate of the cyclopentadienyl ligand displaced during reactions 5 was established by isolation and characterization of the byproduct $[(C_5H_5)PMe_3]I$. Similar salts have been previously prepared.[14]

---

(9) Hunter, A. D.; Legzdins, P. *Organometallics* **1986**, *5*, 1001.

(10) Hunter, A. D.; Legzdins, P.; Martin, J. T.; Sânchez, L. *Organomet. Synth.* **1986**, *3*, 58.

(11) Phosphines that are less basic than PMe_3 only undergo reactions analogous to conversions 3 and 4 when treated with the $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ dimers.[9]

(12) King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1977**, 429.

(13) (a) Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1975**, *14*, 1875. (b) King, R. B.; Saran, M. S.; Anand, S. P. *Inorg. Chem.* **1974**, *13*, 3038. (c) Barraclough, C. G.; Bowden, J. A.; Colton, R.; Commons, C. J. *Aust. J. Chem.* **1973**, *26*, 241.

(14) (a) Jutzi, P.; Kuhn, M. *J. Organomet. Chem.* **1979**, *177*, 349. (b) Jutzi, P.; Saleske, H.; Nadler, D. *J. Organomet. Chem.* **1976**, *118*, C8.

The nucleophilic displacement reactions[15] summarized by eq 5 proceed through short-lived orange intermediates, which we have not as yet been able to characterize spectroscopically. However, by analogy to the substitution processes outlined in eq 1, we believe that the first step in reactions 5 is probably the formation of an η^1-C_5H_5 complex, the orange intermediate, i.e.

$$[(\eta^5\text{-}C_5H_5)M(NO)I(PMe_3)_2]I + 2PMe_3 \rightarrow [(\eta^1\text{-}C_5H_5)M(NO)(PMe_3)_4I]^+I^- \quad (6)$$

The seven-coordinate cationic complex thus formed could then undergo nucleophilic attack by PMe_3 at the η^1-cyclopentadienyl ring to afford the final products, i.e.

$$[(\eta^1\text{-}C_5H_5)M(NO)(PMe_3)_4I]^+I^- + PMe_3 \rightarrow M(NO)(PMe_3)_4I + [(C_5H_5)PMe_3]I \quad (7)$$

It is interesting to compare reactions 7, in which the C_5H_5 group is formally displaced as a cation, with the transformation involving a valence isoelectronic rhenium reactant, i.e.[4]

$$(\eta^1\text{-}C_5H_5)Re(NO)(PMe_3)_3Me + PMe_3 \rightarrow [Re(NO)(PMe_3)_4Me]^+C_5H_5^- \quad (8)$$

in which the C_5H_5 ligand is liberated from the coordination sphere of the metal as an anion. It thus appears that for these systems, the mode of reactivity of PMe_3 with the cyclopentadienyl-containing reactant is governed by the requirement that the final tetrakis(phosphine) product complexes each satisfy the familiar 18-valence-electron rule.

From a practical point of view, the most convenient method for the synthesis of the $M(NO)(PMe_3)_4I$ complexes is the direct treatment of the $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ (M = Mo, W) dimers with 10 equiv of PMe_3, i.e.

$$[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2 + 10PMe_3 \xrightarrow{CH_3CN} 2M(NO)(PMe_3)_4I + 2[(C_5H_5)PMe_3]I \quad (9)$$

Obviously, reactions 9 are simply the sums of the conversions shown in eq 3–5, and they do afford the desired $M(NO)(PMe_3)_4I$ (M = Mo, W) products in good yields. The characteristic chemistry of these electron-rich nitrosyl complexes is currently being investigated.

In closing, one final point concerning the reactions of the $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ dimers with PMe_3 must be made. In the presence of an added reducing agent such as sodium amalgam, the two reactants do not produce the $M(NO)(PMe_3)_4I$ complexes considered above. Instead, the reaction that occurs under these experimental conditions is as shown in eq 10, i.e.

$$[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2 + 4Na/Hg + 4PMe_3 \xrightarrow{THF} 2(\eta^5\text{-}C_5H_5)M(NO)(PMe_3)_2 + 4NaI + Hg \quad (10)$$

the final $(\eta^5\text{-}C_5H_5)M(NO)(PMe_3)_2$ (M = Mo, W) complexes being isolable in excellent yields as orange, crystalline solids. Conversions 10 are particular examples of a general mode of reactivity that we have described in some detail previously.[9] The new $(\eta^5\text{-}C_5H_5)M(NO)(PMe_3)_2$ compounds are formally related to the $M(NO)(PMe_3)_4I$ complexes and, like them, are very air- and moisture-sensitive and decompose in chlorinated organic solvents. The spectroscopic properties of these compounds (Table I) are consistent with their possessing the familiar "three-legged piano-stool" molecular structures.[9] Of particular interest are the very low nitrosyl-stretching frequencies evident in their IR spectra [e.g. ν_{NO} (CH_2Cl_2) 1523 and 1510 cm^{-1} for M = Mo and W, respectively], a feature that again emphasizes the electron richness of the group 6 metal centers in these complexes.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and a graduate scholarship to A.D.H. In addition, L.S. acknowledges the Spanish Ministry of Education for the award of a postdoctoral fellowship.

Registry No. $(\eta^5\text{-}C_5H_5)Mo(NO)I_2(PMe_3)$, 110015-39-9; $(\eta^5\text{-}C_5H_5)W(NO)I_2(PMe_3)$, 110044-52-5; $[(\eta^5\text{-}C_5H_5)Mo(NO)I(PMe_3)_2]I$, 110015-40-2; $[(\eta^5\text{-}C_5H_5)W(NO)I(PMe_3)_2]I$, 110015-41-3; $Mo(NO)(PMe_3)_4I$, 110015-42-4; $W(NO)(PMe_3)_4I$, 110015-43-5; $(\eta^5\text{-}C_5H_5)Mo(NO)(PMe_3)_2$, 110015-44-6; $(\eta^5\text{-}C_5H_5)W(NO)(PMe_3)_2$, 110015-45-7; $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$, 12203-25-7; $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$, 71341-43-0; $[(C_5H_5)PMe_3]I$, 110015-46-8; PMe_3, 594-09-2.

---

(15) Related displacements of a cyclopentadienyl ligand by other nucleophiles have been reported; for representative examples, see: (a) Mawby, R. J.; White, C. *J. Chem. Soc., Chem. Commun.* **1968**, 312. (b) White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. (c) Kita, W. G.; McCleverty, J. A.; Patel, B.; Williams, J. *J. Organomet. Chem.* **1974**, *74*, C9. (d) McCleverty, J. A.; Williams, J. *Transition Met. Chem.* (*Weinheim, Ger.*) **1976**, *1*, 288. (e) Avilés, T.; Royo, P. *J. Organomet. Chem.* **1981**, *221*, 333. (f) Slocum D. W.; Engelmann, T. R.; Fellows, R. L.; Moronski, M.; Duraj, S. *J. Organomet. Chem.* **1984**, *260*, C21 and references cited therein.

Contribution from the Institute of Industrial Science,
University of Tokyo, 22-1 Roppongi, 7 Chome, Minato-ku, Tokyo 106, Japan

Cis Influence on Nuclear Spin–Spin Coupling Constants and Metal–Ligand Bonding Properties in Tin(II)-Coordinated Transition-Metal Complexes

Tetsu Yamakawa, Hiroshi Moriyama, Sumio Shinoda, and Yasukazu Saito*

Received November 3, 1986

Geminal ^{119}Sn–^{117}Sn nuclear spin–spin coupling constants of transition-metal complexes with chemically equivalent but magnetically nonequivalent trichlorostannate ($SnCl_3^-$) ligands have been satisfactorily correlated with orbital characteristics of the specific occupied and unoccupied molecular orbitals in the Pople–Santry framework by the extended Hückel method. The orbital energy of the axial ligand was important for determining the magnitude of the geminal coupling constants between the trans-disposed tin(II) ligands on the equatorial plane of the octahedral complexes. The ^{99}Ru–^{119}Sn one-bond coupling constants and the bonding properties of the metal–ligand coordination were also discussed from the viewpoint of the cis influence.

Introduction

Nuclear spin–spin coupling constants in coordination compounds provide valuable information not only on the molecular structures,[1,2] static and dynamic, but also on the metal–ligand bonding properties.[3] This molecular information has attracted special

---

* To whom correspondence should be addressed.

(1) Davis, J. A. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, p 813 and references therein.