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Reactions of Nickel, Palladium, and Platinum Complexes with Carbonyl Sulfide

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The complexes ML_3 (M = Ni, Pd, Pt; L = PPh_3, $P(p\text{-}C_6H_4CH_3)_3$) react with carbonyl sulfide to afford $M(CO)L_3$, $M(CO)_2L_2$, $M(\eta^2\text{-}COS)L_2$, and $M(COS_2)L_2$ complexes, depending upon M, L, and reaction conditions. These reactions are contrasted with those involving CS_2 in place of COS. A mechanism for the reductive disproportionation of COS by $Pt(PPh_3)_4$ involving a metal–sulfide intermediate is proposed. The dioxygen complexes $Pt(O_2)L_2$ and $Pd(O_2)L_2$ react with carbonyl sulfide to afford metal thiocarbonates, $Pt(CO_2S)L_2$ and $Pd(CO_2S)L_2$, in which the thiocarbonate ligand is asymmetrically bound to the metal.

Introduction

The complexes ML_3 (M = Ni, Pd, Pt; L = tertiary phosphine) react with CO_2,[1,2] COS,[3,4] and CS_2[4] to afford the compounds $M(\eta^2\text{-}CXS)L_2$ (X = O, S). There appear to be very exacting electronic requirements on the metal–ligand-bonding interaction for formation of a stable complex, as evidenced by the stability of $Ni(\eta^2\text{-}CO_2)(PR_3)_2$ (R = Cy, Et, *n*-Bu) and $M(\eta^2\text{-}CS_2)(PPh_3)_2$ (M = Pd, Pt) and the instability of $Ni(\eta^2\text{-}CS_2)(PR_3)_2$[4,5] and $M(\eta^2\text{-}CO_2)(PR_3)_2$[6,7] (M = Pd, Pt; R = Cy, Ph) complexes. We have been investigating the coordination chemistry and metal-promoted condensation reactions of heteroallene molecules.[8–10] Here we report on the reactions of ML_3 complexes with COS, a molecule that is structurally similar to CO_2 and CS_2 with many intermediate chemical and physical properties.[11]

Experimental Section

All reactions were performed in deoxygenated solvents under an atmosphere of N_2 or COS. Analyses were performed by Microtech Laboratories, Skokie, IL, Gailbrath, Inc., Knoxville, TN, and H. Beck of the Analytical Services Laboratory of Northwestern University. Infrared spectra were recorded on Perkin-Elmer 727B and 283 spectrometers. Phosphorus NMR spectra were obtained on a JEOL Fx90Q spectrometer operating at 36.2 MHz with broad-band ^1H decoupling. Peak positions are relative to 85% phosphoric acid with downfield values reported as positive. Carbonyl sulfide was obtained from the Matheson Gas Co., East Rutherford, NJ. The compound $Ni(CO)_2(PPh_3)_2$ was obtained from Research Organic/Inorganic Chemical Corp., Sun Valley, CA. The complexes $Pt(PPh_3)_4$,[12] $Pt(\eta^2\text{-}COS)(PPh_3)_2$,[4] $Pt_2S(CO)(PPh_3)_3$,[4] $Pt(O_2)(PPh_3)_2$,[7] $Pd(PPh_3)_3$,[13] $Pd(P(p\text{-}C_6H_4CH_3)_3)_3$,[14] and $Ni(PPh_3)_3$[14] were prepared by published procedures.

Syntheses. $Pt(COS_2)(PPh_3)_2$, (Dithiocarbonato)bis(triphenylphosphine)platinum(II). Method A. A solution of $Pt(PPh_3)_4$ (0.176 g in 5 mL of toluene) was stirred under an atmosphere of COS for 22 h. The suspension was combined with 15 mL of hexane, and the pale yellow solid was collected by filtration. The yield was 0.066 g (57%). Recrystallization from $CHCl_3$/hexane gave white crystals of the chloroform-solvated complex; mp 250–253 °C dec. Anal. Calcd for $C_{37}H_{30}OP_2PtS_2\cdot CHCl_3$: C, 49.01; H, 3.36. Found: C, 49.09; H, 3.03. **Method B.** A solution of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ (0.092 g in 5 mL of benzene) was stirred under an atmosphere of COS for 24 h. The suspension was combined with 20 mL hexane, and the pale yellow solid was collected by filtration and dried under vacuum. The yield was 0.067 g (65%). Recrystallization from CH_2Cl_2/hexane afforded a white solid that gave $^{31}P\{^1H\}$ NMR and IR spectra identical with spectra of a sample prepared by method A and with those of an authentic sample.[15] **Method C.** A solution of $Pt_2S(CO)(PPh_3)_3$ (0.0977 g in 5 mL of CH_2Cl_2) was stirred under an atmosphere of COS for 24 h. The volume of the solution was reduced to 2 mL under vacuum, and addition of 10 mL of hexane caused a pale yellow solid to precipitate. The solid was recrystallized from CH_2Cl_2/hexane to afford a white solid that was identified by comparison of spectra to those of an authentic sample.[15] The yield was 0.032 g (33% based on PPh_3). Evaporation of the CH_2Cl_2/hexane filtrate to dryness afforded a yellow solid (ν(CO) = 2025 (vs), 1987 (m) cm^{-1}) that was not identified.

$Pt(CO_2S)(PPh_3)_2$, (Thiocarbonato)bis(triphenylphosphine)platinum(II). Carbonyl sulfide was bubbled through a solution of $Pt(O_2)(PPh_3)_2$ (0.15 g in 5 mL of toluene) for 5 min. The solution was combined with 25 mL of hexane, and the tan solid that formed was collected by filtration. Recrystallization from $CHCl_3$/hexane afforded a cream white solid. The yield was 0.12 g (71%). Anal. Calcd for $C_{37}H_{30}O_2P_2PtS\cdot CHCl_3$: C, 49.87; H, 3.41; S, 3.50. Found: C, 48.98; H, 3.33; S, 3.93.

$Pt(\eta^2\text{-}CS_2)(PPh_3)_2$. A CS_2 solution (0.5 mL of CS_2 in 5 mL of toluene) was syringed onto 46.4 mg of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ under an atmosphere of N_2, and the solution was stirred for 10 min. Addition of 10 mL of hexane precipitated an orange solid from solution. The solid was collected by filtration, washed with hexane, and dried under vacuum. The yield was 34.4 mg (73%). The product gave $^{31}P\{^1H\}$ NMR and IR spectra that were identical with those of an authentic sample.[4]

$Pd(\eta^2\text{-}COS)(P(p\text{-}C_6H_4CH_3)_3)_2$. A suspension of $Pd(P(p\text{-}C_6H_4CH_3)_3)_3$ (0.379 g, 0.37 mmol, in 20 mL of hexane) was cooled to 0 °C. Carbonyl sulfide was blown over the stirred solution for 30 min. The suspension was filtered under N_2, and the solid was washed with hexane and dried under vacuum. The yield was 0.258 g (89%). The complex is an air-sensitive tan solid, which is unstable in solution. Anal. Calcd for $C_{43}H_{42}OP_2PdS$: C, 66.62; H, 5.46; P, 7.99; S, 4.14. Found: C, 66.71; H, 5.47; P, 7.64; S, 3.70.

$Pd(COS_2)(P(p\text{-}C_6H_4CH_3)_3)_2$. A sample of $Pd(\eta^2\text{-}COS)(P(p\text{-}C_6H_4CH_3)_3)_2$ (0.320 g, 0.41 mmol) was added to a solution of COS in toluene (~21 mmol of COS in 25 mL of toluene) at −45 °C. When the solution was warmed to 25 °C, the solid dissolved to give an orange

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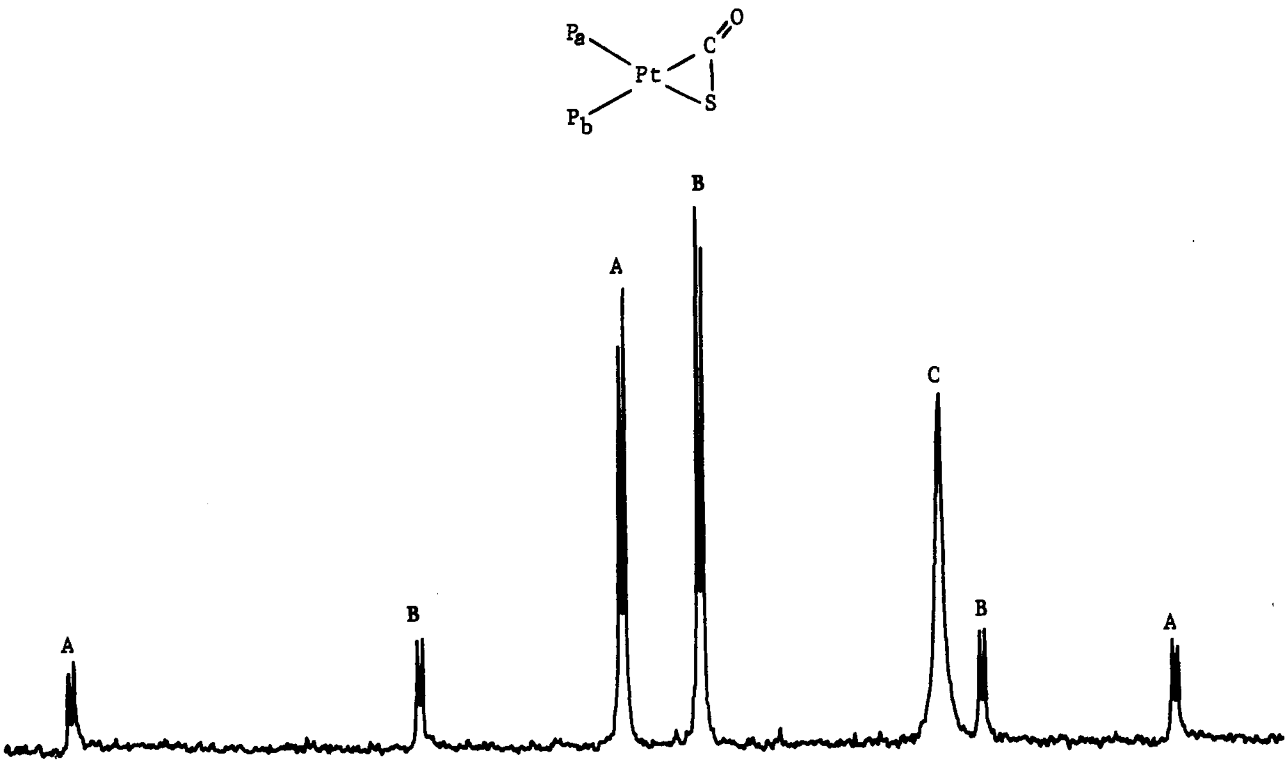

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ generated in situ from $Pt(PPh_3)_3$ and COS: A, P_a resonance; B, P_b resonance; C, PPh_3 resonance. Once isolated from solution, $Pt(\eta^2\text{-}COS)(PPh_3)_2$ is only sparingly soluble in toluene. See Table I for values of δ and J.

solution. The solution volume was reduced to 1 ml under vacuum, and addition of 20 mL of absolute ethanol precipitated a yellow solid. The product was recrystallized from toluene/hexane at −25 °C. The yield was 0.080 g (22%). Anal. Calcd for $C_{43}H_{42}OP_2PdS_2{\cdot}C_6H_5CH_3$: C, 66.77; H, 5.60. Found: C, 66.51; H, 5.59. The complex is also formed from addition of excess COS to $Pd(P(p\text{-}C_6H_4CH_3)_3)_3$ in acetone or tetrahydrofuran.

Attempted Synthesis of $Pd(\eta^2\text{-}COS)(PPh_3)_2$. A hexane suspension of $Pd(PPh_3)_3$ was stirred under an atmosphere of COS for 15 h. The brown solid was collected by filtration and dried under vacuum. The infrared spectrum of the solid exhibits a band at 1740 cm^{-1} (vs), which we attribute to the ketonic carbonyl stretch of $Pd(\eta^2\text{-}COS)(PPh_3)_2$. Analytically pure samples could not be obtained by this method, and attempts to separate the product from $Pd(PPh_3)_3$ by extraction or recrystallization resulted in decomposition. Addition of COS to an acetone solution of $Pd(PPh_3)_3$ gave $Pd(COS_2)(PPh_3)_2$[15] in low yield.

$Pd(CO_2S)(P(p\text{-}C_6H_4CH_3)_3)_2$. Upon exposure to COS a solution of $Pd(O_2)(P(p\text{-}C_6H_4CH_3)_3)_2$ (0.10 g in 5 mL of toluene) turned from pale green to brown and a yellow solid precipitated. Addition of 15 mL of hexane caused further precipitation of the product. The solid was collected by filtration, washed with hexane, and dried under vacuum. The yield was 0.064 g (60%). Anal. Calcd for $C_{43}H_{42}O_2P_2PdS$: C, 65.27; H, 5.35; S, 4.05. Found: C, 64.56; H, 5.29; S, 4.10.

$Ni(CO)(PPh_3)_3$. A suspension of $Ni(PPh_3)_3$ (0.260 g in 10 mL of hexane) was cooled to 0 °C and then exposed to 1 atm of COS for 5 min. After an additional 10 min, the suspension was filtered, and the yellow solid was washed with hexane and dried under vacuum. The yield was 0.158 g (59%). The compound was identified by comparison of physical and spectral data with previously published data.[16,17]

$Ni(CO)_2(PPh_3)_2$. A suspension of $Ni(PPh_3)_3$ (0.255 g in 10 mL of hexane) was stirred under an atmosphere of COS for 10 min. The suspension was filtered, and the compound was recrystallized from toluene/hexane to afford a white solid. The yield was 0.179 g (93%). The compound was identified by comparison of ^{31}P NMR and IR spectra with those of an authentic sample.

Results

Pt Complexes. A hexane suspension of $Pt(PPh_3)_3$ reacts with COS to afford $Pt(\eta^2\text{-}COS)(PPh_3)_2$,[4] the first reported metal–carbonyl sulfide complex. Addition of excess COS to $Pt(PPh_3)_3$ in acetone has been reported to yield a bis(carbonyl sulfide) complex, $Pt(COS)_2(PPh_3)_2$.[3] On the other hand, we find that $Pt(PPh_3)_3$ or $Pt(PPh_3)_4$ reacts with excess COS to afford a dithiocarbonate:

$$Pt(PPh_3)_4 + COS\ (\text{excess}) \rightarrow Pt(COS_2)(PPh_3)_2 \quad (1)$$

The similarity of the analytical and spectroscopic data to those reported for "$Pt(COS)_2(PPh_3)_2$" led us to suggest that this complex be reformulated as $Pt(COS_2)(PPh_3)_2$.[18]

The $^{31}P\{^1H\}$ NMR spectrum of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ consists of an AB spin pattern that is consistent with the structure proposed for the complex[4] (see Figure 1). The values of J and δ (Table I) are very similar to those of $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$, and thus the environments of the phosphorus nuclei in the two complexes are similar. Although the mode of attachment of COS and CS_2 to the PtL_2 metal center is the same, the strength of the C═S bond is not, as evidenced by the reactivity of the COS complex (vide infra) and the stability of the CS_2 complex. The $^{31}P\{^1H\}$ NMR spectrum of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ is invariant to temperature up to the point where decomposition becomes significant ($\sim$−20 °C), and thus no fluctional processes of the COS ligand occur on the NMR time scale. Similarly, the CS_2 complex is rigid on the NMR time scale,[19] whereas $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ is fluctional above −50 °C.[6] The ability of olefins to accept electron density from NiL_3 complexes has been correlated with the strength of the bonding interaction.[20] The electron affinities of CS_2, COS, and CO_2 (1.0, 0.46, −0.6 eV, respectively)[21] correlate well with the

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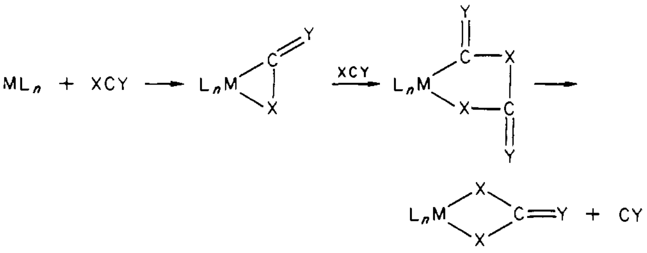
Table I. ^{31}P NMR Data for the Complexes

	T, °C	δ	^2J(PP), Hz	J(^{195}Pt-^{31}P), Hz
$Ni(CO)(PPh_3)_3$^{a}	−75	31.4		
$Ni(CO)_2(PPh_3)_2$^{a}	−75	32.8		
Pt(η^2-COS)($PPh_3)_2$^{a}	−75	21.5 P_b^{f}	24.4	2471
		31.2 P_a		4817
Pt(η^2-CS_2)($PPh_3)_2$^{b}	30	21.2 P_b^{f}	22.0	2792
		33.1 P_a		4883
Pd(η^2-COS)(P(p-$C_6H_4CH_3)_3)_2$^{c,d}	−60	22.2	37.0	
		27.5		
$Pd(CO_2S)$(P(p-$C_6H_4CH_3)_3)_2$^{e}	30	28.0	34.2	
		23.0		
$Pd(COS_2)$(P(p-$C_6H_4CH_3)_3)_2$^{e}	−45	27.6		
$Pt(COS_2)(PPh_3)_2$^{e}	−45	16.6		3162
$Pt(CO_2S)(PPh_3)_2$^{e}	−40	6.4 P_b^{f}	22.5	3343
		21.1 P_a		3000

^{a} Toluene-d_8. ^{b} C_6D_6/CS_2. ^{c} Acetone-d_6. ^{d} Assignments tentative, extensive decomposition occurs upon dissolution. ^{e} $CDCl_3$. ^{f} P_a assigned to the phosphorus atom trans to sulfur on the basis of the magnitude of J(^{195}Pt-^{31}P).

Scheme I. Proposed Mechanism of Metal-Promoted Reductive Disproportionations of Heteroallenes^a



^{a} Depending on the nature of Y, the fragment CY may remain coordinated to the metal.

Scheme II. Proposed Mechanism of the Reductive Disproportionation of COS by PtL_4 (L = PPh_3)

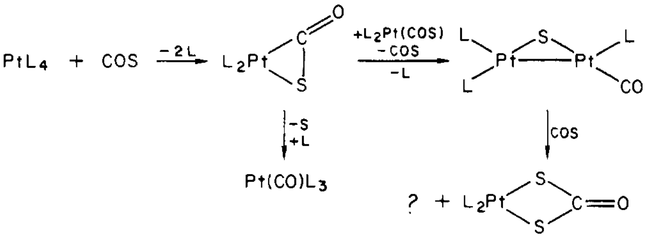


Table II. Infrared Data of the Complexes^a

compd	ν(C=O) or ν(C=S)	$\nu(\overline{\text{MCS}})$	ν_{as}(C-S)^b
Pd(η^2-COS)(P(p-$C_6H_4CH_3)_3)_2$	1756 (s, sh)	630 (s)	
	1739 (vs)		
Pd(η^2-COS)($PPh_3)_2$	1740 (vs)	639 (m)	
$Pd(COS_2)$(P(p-$C_6H_4CH_3)_3)_2$	1680 (vs, br)		832 (s)
	1610 (vs)		
$Pd(CO_2S)$(P(p-$C_6H_4CH_3)_3)_2$	1631 (vs)		876 (w)
			850 (w)
Pt(η^2-COS)($PPh_3)_2$	1730 (vs)	630 (s)	
Pt(η^2-CS_2)($PPh_3)_2$	1155 (vs)	650 (s)	
	1147 (vs)		
$Pt(COS_2)(PPh_3)_2$	1688 (vs, br)		835 (s)
	1615 (vs)		
$Pt(CO_2S)(PPh_3)_2$	1634 (vs)		875 (w)
			849 (w)
$Pt_2S(CO)(PPh_3)_3$	2009 (vs)		
	1983 (sh)		
	1995 (vs)^c		
$Ni(CO)(PPh_3)_3$	1927 (vs)		
$Ni(CO)_2(PPh_3)_2$	2005 (vs)		
	1940 (vs)		

^{a} Nujol mulls except where noted; all values in cm^{-1}. ^{b} See ref 15. ^{c} In toluene.

observed reactivity of these ligands toward basic metal complexes, and the fluctional behavior of the CO_2 complex is probably a reflection of the weaker back donation to the C=O-bound ligand.

Equation 1 represents a metal-promoted reductive disproportionation of COS. Examples of metal-promoted disproportionations of CO_2,[22,23] CS_2,[24] RNCO,[25,26] RNCS,[27,28] and RNCNR[29] have been reported, and in each case the intermediacy of a head-to-tail bis(heteroallene) dimer has been proposed (see Scheme I). In instances where head-to-tail dimers have been isolated,[28,30-32] they are stable and do not rearrange. Our studies have demonstrated that C=S bond cleavage is a facile process in metal-(η^2-COS) complexes and that such complexes are less stable toward dissociation and decomposition than the related CS_2 complexes.[18,33,34] If reaction 1 proceeds by the mechanism depicted in Scheme I, we would expect formation of the head-to-tail dimer to be fast since Pt(η^2-COS)($PPh_3)_2$ decomposes if allowed to stand in solution, and rearrangement of the head-to-tail dimer would be the rate-determining step. Our failure to detect and isolate this proposed intermediate, $Pt(COS)_2(PPh_3)_2$, leads us to propose that reaction 1 proceeds by the alternative mechanism shown in Scheme II. Reaction 1 was monitored by IR (Table II) and ^{31}P NMR spectroscopy (Table I). When COS is added to a toluene solution of $Pt(PPh_3)_4$, Pt(η^2-COS)($PPh_3)_2$ is formed (ν(CO) = 1730 cm^{-1}). Within 30 min the ketonic carbonyl stretch disappears and there appears a new band at 1995 cm^{-1}, characteristic of $Pt_2S(CO)(PPh_3)_3$. After several hours this band begins to decrease in intensity and bands characteristic of $Pt(S_2CO)(PPh_3)_2$ appear (ν(C=O) = 1685, 1610 cm^{-1}). Because of the extensive splitting of the phosphorus resonances of $Pt_2S(CO)(PPh_3)_3$, owing to the presence of three inequivalent phosphorus nuclei and four isotopomers of ^{195}Pt, the dimer was not observed by ^{31}P NMR spectroscopy.[35] After 1 h the formation of $Pt(COS_2)(PPh_3)_2$ was detected by NMR methods. The dithiocarbonate can be prepared from $Pt(PPh_3)_4$, Pt(η^2-COS)($PPh_3)_2$, or $Pt_2S(CO)(PPh_3)_3$ by addition of COS (see Experimental Section). These spectroscopic and chemical results support the proposed mechanism (Scheme II).[36]

The formation of $Pt(CO)(PPh_3)_3$ was also detected spectroscopically (ν(CO) = 1940 cm^{-1}; δ 12.4 (J = 3574 Hz))[37,38] when the addition of COS was performed at room temperature, whereas addition of COS to a solution of $Pt(PPh_3)_4$ at

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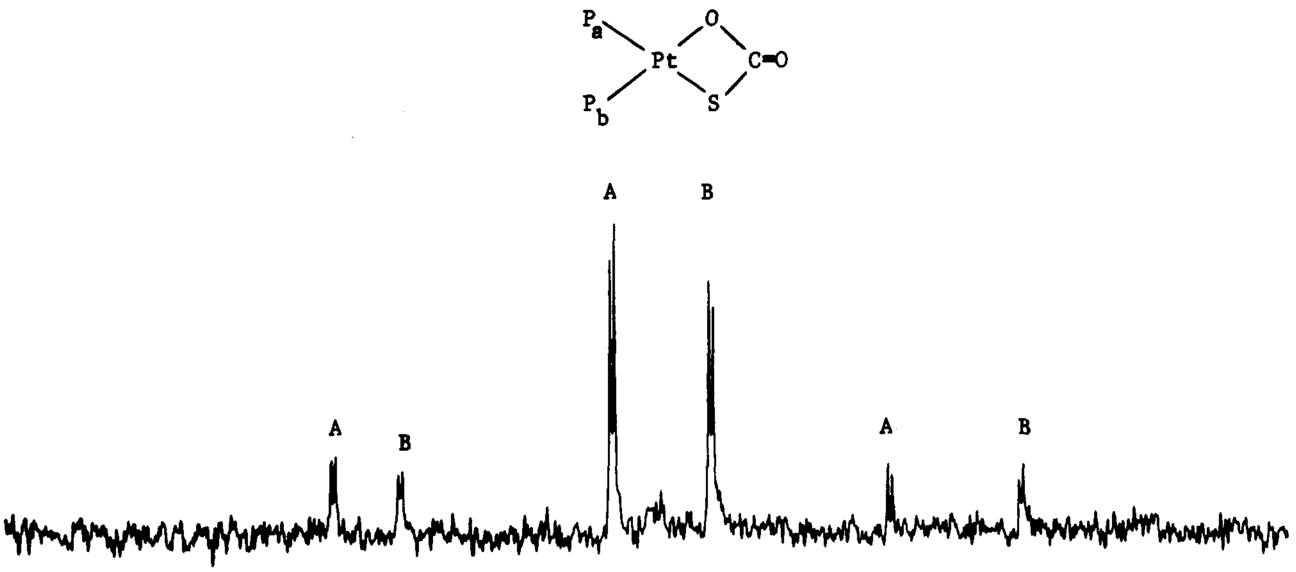


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $Pt(CO_2S)(PPh_3)_2$: A, P_a resonance; B, P_b resonance. See Table I for values of δ and J.

−75 °C yields only $Pt(\eta^2\text{-}COS)(PPh_3)_2$ and PPh_3. If the reaction mixture is warmed to room temperature some $Pt(CO)(PPh_3)_3$ is formed, but the major product is $Pt_2S(CO)(PPh_3)_3$. The ratio $Pt(CO)(PPh_3)_3/Pt_2S(CO)(PPh_3)_3$ increases as the temperature of the reaction increases. Presumably, the decomposition of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ via sulfur elimination to afford $Pt(CO)(PPh_3)_3$ is kinetically competitive with the dimerization reaction at higher temperatures. The fate of the sulfur in this carbonylation reaction has not been determined, but abstraction by PPh_3 to give $SPPh_3$ apparently is not significant since no $SPPh_3$ was detected.

Addition of CS_2 in toluene to $Pt(\eta^2\text{-}COS)(PPh_3)_2$ results in the formation of $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$. This ligand-exchange process must be facile since if $Pt(\eta^2\text{-}COS)(PPh_3)_2$ remained in solution long enough to dimerize, $Pt(CS_3)(PPh_3)_2$ would be formed.

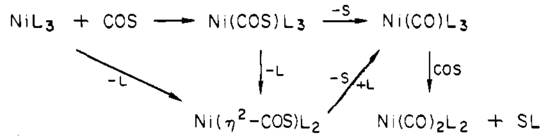
The dioxygen complexes $Pt(O_2)(PPh_3)_2$ and $Pd(O_2)(PPh_3)_2$ react with CS_2 to afford $Pt(COS_2)(PPh_3)_2$ and $Pd(COS_2)(PPh_3)_2$,[15a] and $Pt(O_2)(PPh_3)_2$ reacts with CO_2 to afford a metal peroxycarbonate that decomposes to give $Pt(CO_3)(PPh_3)_2$.[39]

Carbonyl sulfide also reacts with these dioxygen complexes. On the basis of the analytical and NMR data, we cannot distinguish whether a monothiocarbonate complex or a peroxymonothiocarbonate is formed. The infrared spectra of the analogous carbonates and peroxycarbonates have been reported.[15a] The similarity of the IR spectra of these complexes (see Table II) to those reported for the carbonates, along with the absence of any band that might be assigned to an O–O stretch, which is present in the spectra of the peroxycarbonate complexes, leads us to suggest that the monothiocarbonate complexes are formed. These are the first examples of transition-metal monothiocarbonate complexes. The formation of triphenylphosphine oxide upon the addition of COS to $Pt(O_2)(PPh_3)_2$ was not detected via NMR spectroscopy.

The $^{31}P\{^1H\}$ NMR spectra of $Pt(CO_2S)(PPh_3)_2$ and $Pd(CO_2S)(P(p\text{-}C_6H_4CH_3)_3)_2$ exhibit AB patterns (see Figure 2), consistent with coordination of the thiocarbonate ligand through one oxygen atom and the sulfur atom in an asymmetric fashion.

Pd Complexes. The reaction of $Pd(PPh_3)_3$ or $Pd(PPh_3)_4$ with COS results in the formation of $Pd(\eta^2\text{-}COS)(PPh_3)_2$. However, the reaction is slow and does not proceed to completion, and the instability of the product has precluded the isolation of analytically pure samples. The slightly more basic complex, $Pd(P(p\text{-}C_6H_4CH_3)_3)_3$, reacts with COS to afford $Pd(\eta^2\text{-}COS)(P(p\text{-}C_6H_4CH_3)_3)_2$ as an analytically pure solid. The complex is unstable in solution, even at −78 °C. When $Pd(\eta^2\text{-}COS)(P(p\text{-}C_6H_4CH_3)_3)_2$ is dissolved at low temperature in COS-saturated toluene, $Pd(COS_2)(P(p\text{-}C_6H_4CH_3)_3)_2$ is formed in low yield, but in contrast to the reactions with the Pt complexes, decomposition is extensive and pure samples of the dithiocarbonate could not be prepared by this method.

Scheme III. Possible Pathways to the Stepwise Carbonylation of NiL_3 by COS ($L = PPh_3$)



Ni Complexes. The reaction of $Ni(PPh_3)_3$ with COS was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Upon addition of 5 equiv of COS to a toluene solution of $Ni(PPh_3)_3$ at −75 °C, the color faded from dark red to yellow, and the $^{31}P\{^1H\}$ resonance of $Ni(PPh_3)_3$ was replaced by a new resonance that we attribute to $Ni(CO)(PPh_3)_3$.[40] The solution was then warmed to room temperature, and the color faded to pale yellow. The ^{31}P resonance of $Ni(CO)(PPh_3)_3$ disappeared, and resonances of $Ni(CO)_2(PPh_3)_2$, PPh_3, and $SPPh_3$ were observed. These results are consistent with the stepwise carbonylation of $Ni(PPh_3)_3$ by COS shown in Scheme III; however, no sulfur-containing metal intermediates were observed. Although $SPPh_3$ is formed, the presence of PPh_3 after all of the $Ni(CO)(PPh_3)_3$ had been converted to $Ni(CO)_2(PPh_3)_2$ demonstrates that sulfur is not quantitatively abstracted by PPh_3, and there are likely to be several paths of sulfur elimination from the proposed intermediates. The complex $Ni(CO)(PPh_3)_3$ can be isolated if the reaction is performed in hexane at 0 °C, whereas at 25 °C the product is $Ni(CO)_2(PPh_3)_2$ (see Experimental Section). Formation of $Ni(CO)(PPh_3)_3$ could proceed through formation of $Ni(COS)(PPh_3)_3$ as an intermediate, which could then eliminate

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(39) The platinum carbonate is formed from a platinum peroxycarbonate by phosphine abstraction of an oxygen atom. See ref 15a.

(40) We have prepared $Ni(CO)(PPh_3)_3$ by the addition of carbon monoxide to $Ni(PPh_3)_3$ at −83 °C, and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture is identical with the spectrum observed when COS is employed as the carbonylating agent. If the solutions of $Ni(CO)(PPh_3)_3$ are warmed to room temperature, $Ni(CO)_2(PPh_3)_2$ and PPh_3 are formed, and $SPPh_3$ is also produced when COS is the carbonylating agent.

sulfur to give Ni(CO)(PPh$_3$)$_3$ or PPh$_3$ to afford Ni(η^2-COS)(PPh$_3$)$_2$. A similar mechanism has been proposed for the formation of Ni(η^2-CO$_2$)(L)$_2$ (L = PEt$_3$, P(n-Bu)$_3$),[2] and the presence of Ni(CO$_2$)(L)$_3$ has been detected spectroscopically. The complex Ni(η^2-CO$_2$)(L)$_2$ is stable, whereas similar reactions with COS afford a mixture of metal carbonyls.[5]

Discussion

The stability of the species M(η^2-COS)(L)$_2$ (L = PPh$_3$) decreases in the order Pt > Pd > Ni. The platinum complex is stable in solution at low temperature, the palladium complex is stable in the solid state but decomposes upon dissolution, and the nickel complex has not been observed, although it is likely to be a transient intermediate in the observed carbonylation reaction. The reactions of ML$_3$ complexes with COS depend on the affinity of the metal center for carbon monoxide and sulfur, the species into which COS fragments upon C=S bond cleavage. Palladium and platinum have a higher affinity for sulfur than does nickel, and the formation of dithiocarbonates is favored. Nickl(0) complexes have a high affinity for π-acceptor ligands (e.g., Ni(CO)$_4$ is stable, Pt(CO)$_4$ is not), and Ni(PPh$_3$)$_3$ selectively binds the CO fragment. Although the preference of the metal center for a π-acceptor rather than a σ-donor ligand may be important in these reactions, kinetic factors are also important, as evidenced by the increased formation of Pt(CO)(PPh$_3$)$_3$ at higher temperature.

It is interesting that Pt$_2$S(CO)(PPh$_3$)$_3$ reacts with CS$_2$ to afford Pt(CS$_3$)(PPh$_3$)$_2$,[35] but addition of CS$_2$ to Pt(PPh$_3$)$_4$ affords Pt(η^2-CS$_2$)(PPh$_3$)$_2$.[4] This complex is stable, and C–S bond cleavage to give Pt$_2$S(CS)(PPh$_3$)$_3$ does not occur. Hence, it is the greater stability of the coordinated C=S bond of CS$_2$ that prevents the formation of Pt(CS$_3$)(PPh$_3$)$_2$ from Pt(PPh$_3$)$_4$ and CS$_2$ by a pathway analogous to Scheme III. Both Pt(S$_2$CNR)(PPh$_3$)$_2$ and Pt(S$_2$CNR)(RNC)(PPh$_3$) are formed from the reaction of Pt(PPh$_3$)$_4$ with SCNR (R = Me, Ph).[41] This reaction might proceed by a mechanism analogous to the one depicted in Scheme III. Cleavage of the dimer at both Pt–S bonds would account for the formation of both products.

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Registry No. Pt(COS$_2$)(PPh$_3$)$_2$, 25787-94-4; Pt(CO$_2$S)(PPh$_3$)$_2$, 81178-19-0; Pt(η^2-CS$_2$)(PPh$_3$)$_2$, 15308-68-6; Pd(η^2-COS)(P(p-C$_6$H$_4$CH$_3$)$_3$)$_2$, 81178-20-3; Pd(COS$_2$)(P(p-C$_6$H$_4$CH$_3$)$_3$)$_2$, 81178-21-4; Pd(η^2-COS)(PPh$_3$)$_2$, 81178-22-5; Pd(CO$_2$S)(P(p-C$_6$H$_4$CH$_3$)$_3$)$_2$, 81178-23-6; Ni(CO)(PPh$_3$)$_3$, 15376-83-7; Ni(CO)$_2$(PPh$_3$)$_2$, 13007-90-4; Pt(η^2-COS)(PPh$_3$)$_2$, 10210-51-2; Pt$_2$S(CO)(PPh$_3$)$_3$, 27664-43-3; Pt(PPh$_3$)$_4$, 14221-02-4; Pt(O$_2$)(PPh$_3$)$_2$, 15614-67-2; Pd(P(p-C$_6$H$_4$CH$_3$)$_3$)$_3$, 27903-26-0; Pd(PPh$_3$)$_3$, 28516-49-6; Pd(O$_2$)(P(p-C$_6$H$_4$CH$_3$)$_3$)$_2$, 81178-24-7; Ni(PPh$_3$)$_3$, 25136-46-3; COS, 463-58-1.

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Notes

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Reactions of Tetrasulfur Tetranitride [Cyclotetra(azathiene)] with Some Tin(II) and Tin(IV) Compounds

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Tetrasulfur tetranitride [cyclotetra(azathiene)] forms adducts with main-group and transition-metal halides.[1,2] Reactions in inert solvents precipitate complexes in which S$_4$N$_4$ acts as a mono- or bidentate ligand. In certain cases the products are adducts of disulfur dinitride. X-ray structures of S$_4$N$_4$·BF$_3$,[3] S$_4$N$_4$·SbCl$_5$,[4] and S$_4$N$_4$·AsF$_5$[5] show unidentate donation through the nitrogen atom. In S$_4$N$_4$·CuCl pairs of S$_4$N$_4$ molecules act as bridging ligands between CuCl chains through 1,3-nitrogen atoms.[6]

Reaction between S$_4$N$_4$ and SnCl$_4$ was first reported at the turn of the century[7,8] to give a red precipitate of stoichiometry SnCl$_4$·2S$_4$N$_4$, and this has been confirmed by more recent work.[10,11] The bromine analogue, SnBr$_4$·2S$_4$N$_4$, forms from S$_4$N$_4$H$_4$ in ether or directly from S$_4$N$_4$ in hydrocarbon solvents.[11] Tin(II) chloride, on the other hand, has been reported to reduce S$_4$N$_4$ to S$_4$N$_4$H$_4$ in alcohol in early work[8] or to give no reaction in ether after 48 h at room temperature.[10]

The availability of more reactive tin(II) species such as dimethoxyltin(II) and bis(dimethylamino)tin(II) and spectroscopic techniques such as tin-119m Mössbauer spectroscopy has prompted us to reinvestigate the chemistry of S$_4$N$_4$ and tin.

Experimental Section

Tetrasulfur tetranitride was prepared by the method of Jolly.[12] Anhydrous SnCl$_2$, SnBr$_2$, and SnCl$_4$ were obtained from Alfa Inorganics, Beverly, MA, and anhydrous SnBr$_4$ was obtained from Apache Chemicals, Rockford, IL, and used without further purification. Tin(II) dimethoxide was prepared from SnCl$_2$,[13] and bis(dimethylamino)tin(II) was prepared by the method of Zeldin.[14] Carbon tetrachloride and dichloromethane were of reagent grade quality and were further dried over P$_4$O$_{10}$. Infrared spectra were recorded on a Beckman IR-12 spectrometer as Nujol or halocarbon mulls, and Mössbauer spectra were recorded with constant acceleration, cam-drive and Ranger Engineering instruments and were recorded vs. Ca^{119m}SnO$_3$ both as the source and standard for zero velocity at room temperature. All reactions were carried out in an inert atmosphere of dry nitrogen. Tin was determined gravimetrically as SnO$_2$, and halogens, nitrogen, carbon, and hydrogen were determined by

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