Organometallics **1989**, *8*, 2367–2371

Christchurch, New Zealand, for recording for us the crystallographic data on compound $[(R^*,R^*),(R^*)]$-**3**·0.5CH_2Cl_2.

Registry No. (R^*,R^*)-**1**, 113587-85-2; (S,S)-**1**, 122331-51-5; (R^*,R^*)-**2**, 113587-95-4; (R^*,R^*)-**3**, 113572-53-5; $[(S,S),(R)]$-**3**, 113666-19-6; $[(S,S),(S)]$-**3**, 113666-17-4; (R^*,R^*)-**3**·0.5CH_2Cl_2, 113572-54-6; (R^*,R^*)-**4**, 116994-76-4; (R^*,R^*)-**5**, 122270-80-8; (R^*,R^*)-**6**, 116994-74-2; (R^*,R^*)-**7**, 122270-82-0; (R^*,R^*)-**8**, 113572-55-7; (R^*,R^*)-**9**, 122270-83-1; (R^*,R^*)-**10**, 122270-84-2; (R^*,R^*)-**11**, 122270-85-3; $[(\eta^5-C_5H_5)Fe(CO)_2Br]$, 12078-20-5; (R^*,R^*)-1,2-$C_6H_4(PMePh)_2$, 122331-49-1; $[R-(R^*,R^*)]$-(+)-1,2-$C_6H_4(PMePh)_2$, 72150-36-8; (±)-PHMePh, 113581-29-6; PH_2Ph, 638-21-1; (±)-PHBnPh, 122270-78-4.

Supplementary Material Available: Crystal data, a view of $[(R^*,R^*),(R^*)]$-**3**·0.5CH_2Cl_2, full tables of bond lengths and angles, and tables of anisotropic thermal factors, final atomic coordinates, and calculated hydrogen atom parameters for $[(R^*,R^*),(R^*)]$-**3**·0.5CH_2Cl_2 (12 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Scope and Mechanism of Oxidative Addition of C=S Bonds to Trinuclear Platinum and Palladium Complexes

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Received March 8, 1989

The coordinatively unsaturated complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$) reacts with the heterocumulenes S=C=E, where E = N^-, O, S, or NR, to give the corresponding adducts $[Pt_3(S{=}C{=}E)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, followed by oxidative addition of the C=S bond and loss of CO to give the products $[Pt_3(\mu_3\text{-}S)(C{\equiv}E)(\mu\text{-dppm})_3]^{2+}$. These products were characterized by elemental analysis and multinuclear NMR spectroscopy. A further intermediate, identified by ^{31}P and ^{13}C NMR as $[Pt_3(\mu_3\text{-}S)(CO)(\mu\text{-dppm})_3]^{2+}$, was formed in the cases where E = O or NR but not when E = S or N^-. The complex $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ reacts with CS_2 to give a complex that was tentatively identified as $[Pd_3(\mu\text{-}CS_2)(\mu\text{-dppm})_3]^{2+}$. In these reactions, the nuclearity of the complexes is maintained by the bridging dppm ligands, and this leads to important differences from related chemistry of other Pt_3 and Pd_3 clusters. The reaction of $[M_3(SCN)(\mu\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ to give $[M_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]^+$ and CO is retarded by free CO, under conditions of either thermal (M = Pd) or photochemical (M = Pt) activation, and the thermal reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ with CS_2 is also retarded by free CO. Two different mechanisms of reaction are throught to operate, and these are discussed.

Introduction

The reactions of the heterocumulenes CS_2 and COS with low oxidation state platinum complexes have been studied thoroughly. Complexes with η^2-C,S binding are formed first, but cleavage of a C=S bond can then occur to give coordinated S and CS or CO.[1-5] The C=S bond cleavage requires a second platinum(0) center, and the favored reaction sequence is shown in Scheme I (E = S or O, L = tertiary phosphine).[5] Carbon disulfide causes fragmentation of the trinuclear cluster $[Pt_3(\mu\text{-}CO)_3L_3]$ (L = P-*t*-Bu_2Ph) to give $[Pt_2(\mu_2\text{-}\eta^3\text{-}CS_2)_2L_2]$ or $[Pt_2(\mu\text{-}S)(CO)_2L_2]$ and adds to the Pt–Pt bond of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$) to give $[Pt_2Cl_2(\mu_2\text{-}\eta^2\text{-}CS_2)(\mu\text{-dppm})_2]$.[6-8] It was of interest to extend this chemistry to studies with the locked trinuclear clusters $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (M = Pd, or Pt), which are much more stable to fragmentation than the clusters $[Pt_3(\mu\text{-}CO)_3L_3]$ studied by Farrar and co-workers,[6,7] in the hope that the mechanism of C=S bond cleavage at a cluster center might be clearer if the nuclearity could be maintained by the bridging dppm ligands.

Scheme I

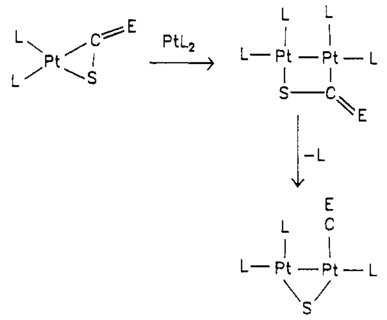

Table I. ^{31}P **NMR Parameters of the Complexes** $[Pt_3(\mu_3\text{-}CO)(SCE)(\mu\text{-dppm})_3]^{2+}$

complex SCE	$\delta(^{31}P)$, ppm	$^1J(PtP)$, Hz
	−9.1	3710
SCN^-	−17.7	3670
COS	−16.4	3380
MeNCS	−16.7	3714
t-BuNCS	−16.7	3660
PhNCS	−17.1	3570

It has been shown that thiocyanate adds to the complexes $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ to give an adduct $[M_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$, which then undergoes CS bond cleavage to give $[M_3(\mu_3\text{-}S)CN(\mu\text{-dppm})_3]^+$.[9] The C=S bond cleavage of SCN^- and RNCS has been much less studied than that of CS_2 or COS,[1-11] and this work de-

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Table II. ^{31}P NMR Parameters of the Complexes $[Pt_3(\mu_3\text{-}S)X(\mu\text{-dppm})_3]^{2+}$

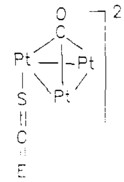
complex X	$\delta(P^a)$	$\delta(P^b)$	$\delta(P^c)$	$^1J(PtP^a)$, Hz	$^1J(PtP^b)$, Hz	$^1J(PtP^c)$, Hz	$^2J(PtP^b)$, Hz	$^3J(P^bP^b)$, Hz
CN^{-}[a]	14.2	−0.3	−13.6	2580	3020	3900	190	170
CS[b]	19.8	0.1	−10.9	2396	3028	4071	162	164
CO[c]	16.8	−0.2	−11.3	2310	3020	4060	150	160
MeNC	15.0	−0.7	−12.4	2410	3020	3980	170	170
t-BuNC	15.2	0.9	−12.5	2420	3040	3980	170	160
PhNC[d]	15.3	0.3	−12.2	2400	3040	3960	170	170

[a] $\delta(Pt^1) = -2909$, $\delta(Pt^2) = -3163$. [b] $\delta(Pt^1) = -2429$, $\delta(Pt^2) = -3122$. [c] $\delta(Pt^1) = -2801$, $\delta(Pt^2) = -3171$, $\delta(^{13}CO) = 164.5$, $^1J(Pt\text{–}C) = 1420$, Hz. [d] $\delta(Pt^1) = -2858$, $\delta(Pt^2) = -3147$.

scribes the reactions of all four reagents.

Results

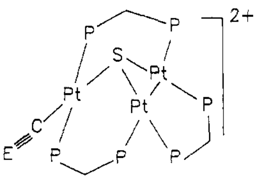
Initial Complexation to the Cluster. All of the reagents studied form initial complexes with $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**1**) in a similar way to that established earlier for SCN⁻. By analogy with this precedent,[9] it is proposed that the complexes have structure **2** with terminal S=C=E group, but, in all cases studied, the ^{31}P NMR spectra of complexes **2** (Table I) gave only a single resonance even at low temperature, and so the complexes must be fluxional. This fluxionality was observed previously for the thiocyanate complex and involves migration of the S=C=E group about the Pt_3 triangle.[9] This fluxionality is significantly faster than the reversible dissociation of the S=C=E group from the adducts **2**, as described.



2a, E=N⁻
2b, E=S
2c, E=O
2d, E=MeN
2e, E=t−BuN
2f, E=PhN

This initial complexation is strong with the ligand SCN⁻ but is weak and reversible for at least some of the neutral reagents. For example, a solution containing **1** and S=C=O at −80 °C gave separate ^{31}P NMR signals due to **1** and **2c** (Table I), but at −20 °C only an average ^{31}P signal was observed due to rapid exchange between **1** and **2c**. Presumably the S=C=O ligand coordination and dissociation are rapid on the NMR time scale at −20 °C and above. For this reason, these initial adducts **2** could not be isolated, but the ^{31}P NMR parameters are so similar to those of the stable SCN⁻ adduct[9] that there is little doubt about the structures. The very much higher stability of the thiocyanate adduct is presumably due to the negative charge on this ligand leading to a much greater ionic attraction to the dicationic **1**.[9] In the case of the ligands RNCS, the equilibrium constant at −80 °C favored **2** and cleavage of the C=S bond occurred at −40 °C.

Characterization of Reaction Products. The initially formed equilibrium mixture of **1** and **2** reacted further at room temperature, and the final products were characterized as $[Pt_3(\mu_3\text{-}S)(CE)(\mu\text{-dppm})_3]^{2+}$ (**3**).



3a, E=N⁻
3b, E=S
3c, E=O
3d, E=MeN
3e, E=t−BuN
3f, E=PhN

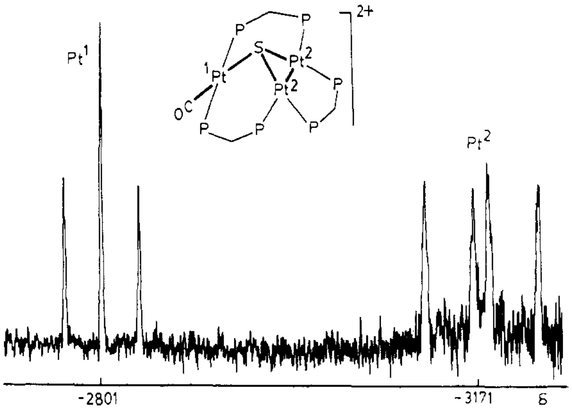


Figure 1. The ^{195}Pt{^{1}H} NMR spectrum (64.3 MHz) of $[Pt_3(\mu_3\text{-}S)(CO)(\mu\text{-dppm})_3]^{2+}$ (**3c**).

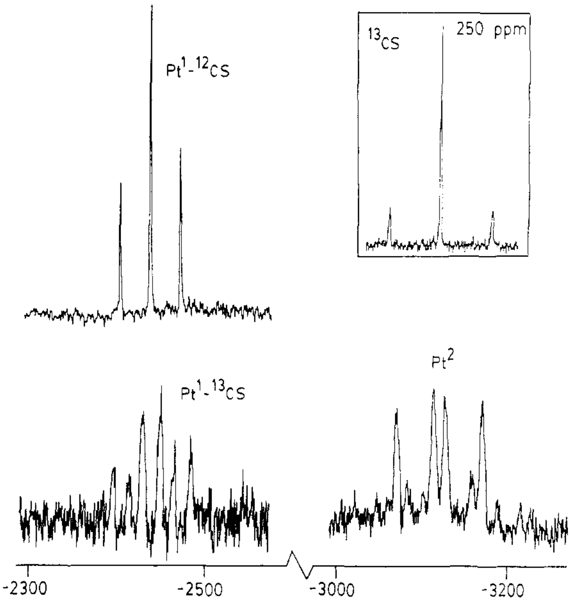


Figure 2. The ^{195}Pt{^{1}H} NMR spectrum (64.3 MHz) of $[Pt_3(\mu_3\text{-}S)(^{13}CS)(\mu\text{-dppm})_3]^{2+}$ (**3b***) and, above, the Pt^1 resonance of the ^{12}CS analogue **3b**. The extra coupling in the lower spectrum is due to $^1J(PtC) = 1333$ Hz. The inset shows the thiocarbonyl resonance in the ^{13}C NMR spectrum (75 MHz) of **3b***, with satellites due to $^1J(Pt^1C) = 1333$ Hz.

The thiocyanate reaction was very slow at room temperature but occurred much more rapidly on photolysis, while the thermal reaction with PhNCS was rapid at room temperature as described above. The resulting complexes were readily characterized by the ^{1}H and ^{31}P NMR spectra, with extra evidence in some cases from ^{195}Pt and ^{13}C NMR spectra (Figures 1 and 2). The structures of the similar complexes $[Pd_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]^+$ and $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$ have been determined crystallographically, and the spectral properties (Table II and Experimental Section) are characteristic of the structures with just one Pt–Pt bond.[9,12]

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Additional spectroscopic data were obtained for **3b** and **3c**. The ^{13}C NMR spectrum of **3b***, prepared from $^{13}CS_2$, gave $\delta(^{13}CS) = 250$ [$^1J(PtC) = 1333$ Hz, $^2J(PC) = 19.3$ Hz] (Figure 2). The chemical shift is lower than for most thiocarbonyl complexes (286–442 ppm),[13] but the literature tabulation contains no platinum thiocarbonyl complexes and the $\delta(^{13}CO)$ values for platinum carbonyls are also lower than for most other metal carbonyls. For example, **3c** has $\delta(^{13}CO) = 164.5$ ppm, with $^1J(PtC) = 1421$ Hz, in the expected range for platinum carbonyls but at lower shift than most metal carbonyls.[14,15] The chemical shift for the $Pt^{13}CS$ is therefore reasonable. The value of $\nu(^{13}C{\equiv}S)$ for **3b*** was 1337 cm^{-1}, and the expected value for **3b** is therefore ~1376 cm^{-1} where it was obscured. This falls in the expected range of $\nu(C{\equiv}S)$ of 1135–1409 cm^{-1}.[13] In particular, the $C{\equiv}S$ stretching frequency of the cationic $[PtCl(CS)(PPh_3)_2]^+$ is at 1400 cm^{-1} while Pt(0) derivatives have $\nu(C{\equiv}S) = 1300$–1310 cm^{-1}.[5,13] Complexes **3c** and **3c*** (^{13}CO) had $\nu(CO) = 2103$ and 2051 cm^{-1}, respectively. Complexes **3d–f** gave $\nu(C{\equiv}NR) = 2249$, 2215, and 2187 cm^{-1}, respectively.

Complexes **3** undergo a fluxional process in solution which leads to an effective plane of symmetry containing the $Pt_3(PCP)_3$ unit. This is demonstrated in the ^1H NMR spectra by equivalence of the $CH^aH^bP_2$ protons of the dppm ligands in the room-temperature ^1H NMR spectra but nonequivalence at low temperature. The effect has been observed previously in $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$ and related complexes and is due to inversion at the μ_3-S unit, giving a planar $Pt_3(\mu_3\text{-}S)(CE)$ transition state.[9,12,16]

Most of complexes **3** were stable, but **3b** and **3c** underwent further reactions. Complex **3b** reacted slowly with excess CS_2 to give a new complex that could not be fully characterized; it was therefore important to isolate **3b** before this reaction occurred. The carbonyl complex **3c** was unstable in solution, especially in moist solvents, when reaction with water to give CO_2 and $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$ occurred. This is a novel example of a well-known reaction of cationic platinum carbonyls.[17]

Further Reaction Intermediates. The course of each of the above reactions was monitored by ^{31}P NMR spectroscopy, and, in some cases, additional intermediates were detected. In the reactions with RNCS to give **3d–f**, the carbonyl complex **3c** was detected at intermediate stages of reaction and then decayed as **3d–f** were formed in essentially quantitative yield. This indicates clearly that the reaction initially gives mostly **3c** and RNC, and the better ligand RNC then displaces CO from **3c** to give **3d–f**.[18] A similar course was followed in the reaction of $[Pt_3(\mu_3\text{-}^{13}CO)(\mu\text{-dppm})_3]^{2+}$ with COS. The product was identified as largely $[Pt_3(\mu_3\text{-}S)(^{13}CO)(\mu\text{-dppm})_3]^{2+}$ (**3c***) by the ^{13}C NMR and IR spectra. The IR spectrum contained peaks due to both $\nu(^{13}CO)$ and $\nu(^{12}CO)$ in a 2.2:1 intensity ratio, which is therefore the ratio of **3c***:**3c** in the isolated product. This is a minimum value for the true selectivity since ^{12}CO (formed by fragmentation of COS) for ^{13}CO exchange in the product or in unreacted **1*** will lead to some scrambling of the label.[20]

Table III. First-Order Rate Constants, k_1, for the Reaction of $[Pd_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ To Give CO and $[Pd_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]^+$

solvent	E_T[a]	$p(CO)$, Torr	T, K	10^5k_1, s^{-1}
MeOH	55.5	0	298	3.61
			303	6.52
			308	12.90
			318	50.0
			324	103
Me_2CO	42.2	0	308	28.1
EtOH	51.9	0	308	13.0
90:10 $MeOH/H_2O$	56.3	0	308	11.0
80:20 $MeOH/H_2O$	57.0	0	308	8.8
70:30 $MeOH/H_2O$	57.8	0	308	8.3
Me_2CO	42.2	0	308	28.1
		127	308	27.3
		184	308	24.8
		200	308	21.4
		329	308	15.9
		476	308	13.6
		754	308	12.7

[a] Reichardt parameter of solvent polarity.

Table IV. Observed First-Order Rate Constants, k_1, for Reaction of $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (M = Pd or Pt) with Excess CS_2 in MeOH at 298.3 K

M	$10^5[M_3]$,[a] L mol^{-1}	$10^2[CS_2]$, L mol^{-1}	10^4k_1, s^{-1}
Pd	17.4	0	0.205[b]
Pd	8.7	5.0	3.11
Pd	9.5	9.0	5.36
Pd	8.7	15.0	10.0
Pd	7.7	16.6	9.8
Pd	8.7	50.0	33.9
Pt	4.1	0	0.31[b]
Pt	4.1	0.332	3.22
Pt	4.1	1.33	6.35
Pt	4.1	3.33	13.6
Pt	4.1	6.66	25.6

[a] $M_3 = [M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$. [b] Apparent rate of decomposition in the absence of CS_2.

The carbonyl complex **3c** was not observed at intermediate stages in the reactions of **1** with CS_2 or SCN^-. This can be rationalized in the former case since free $C{\equiv}S$ is a high-energy species[13] and, if it were formed, it would probably decompose before it could substitute for the carbonyl ligand in **3c***. A different mechanism must therefore be invoked. In this case, no other intermediates were detected. The reaction with SCN^- when monitored by ^{31}P NMR spectroscopy gave at intermediate stages low quantities of a complex, characterized by a singlet resonance at $\delta = -21.0$ ppm with $^1J(PtP) = 3180$ Hz. The concentration of this complex was not high enough at any stage of reaction to allow further data to be obtained, and its identity remains unknown. We note only that the ^{31}P chemical shift is similar to that of adducts of **1** with either anionic or neutral ligands (see Table I).[9,19,20] The complex was not present at the completion of the reaction, and it is not clear from the above evidence if it is a reaction intermediate or if it is formed in a parallel nonproductive equilibrium with complex **1**.

Kinetic Studies. The kinetics of reaction of SCN^- and CS_2 with $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (M = Pd and Pt) were studied. These were the reactions that proceed cleanly for

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(18) In addition, some minor species were observed and these are due to reversible addition of CO and RNC to residual complex **1** or **2**. It has been shown independently that the coordinatively unsaturated 42e clusters add many ligands to give 44e and 46e clusters, and the CO adducts have been described earlier.[19] These minor species decayed in parallel with the decay of **3c**.

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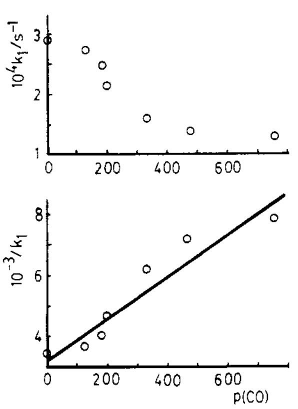


Figure 3. Dependence of the observed first-order rate constants, k_1 (s^{-1}), for reaction of $[Pd_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ in acetone at 35 °C on the pressure of CO (Torr): above, 10^4k_1 vs $p(CO)$; below, $10^{-3}/k_1$ vs $p(CO)$.

both the palladium and platinum complexes and for which complex **3c** was not detected at intermediate stages.

The reaction of $[Pd_3(\mu_3\text{-}CO)(SCN)(\mu\text{-dppm})_3]^+$ to give $[Pd_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]^+$ and CO occurred cleanly, and an isosbectic point at 432 nm was observed when the reaction in methanol was monitored by UV–visible spectrophotometry. The reaction followed first-order kinetics, and, from the rate constants between 25 °C and 51 °C (Table IV) the activation parameters were calculated as $\Delta H^\ddagger = 104 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = 17 \pm 5$ J K^{-1} mol^{-1}. First-order kinetics were also observed in acetone, ethanol, or methanol/water solvents, and the first order rate constants are also given in Table III. The rates are highest in less polar solvents though the range of reactivity from acetone ($k_1 = 2.8 \times 10^{-4}$ s^{-1}) to 70/30 v/v methanol/water ($k_1 = 8.3 \times 10^{-5}$ s^{-1}) is modest. Carbon monoxide retarded the reaction to some extent, as shown by the data in Table IV. Graphs of k_1 and $1/k_1$ vs $p(CO)$ are shown in Figure 3. The dependence of rate on $p(CO)$ is evidently fairly complex, and the mechanistic discussion will depend only on the qualitative observation of CO retardation. NMR studies showed no adduct formation between **2a**, or the Pd_3 analogue, and CO.

The reaction of $[Pt_3(\mu_3\text{-}CO)(SCN)(\mu\text{-dppm})_3]^+$ to give $[Pt_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]^+$ and CO was slow, and so the thermal reaction was not studied in detail. The first-order rate constant in methanol at 25 °C was 1.1×10^{-5} s^{-1}, that is 3.3 times slower than the palladium analogue. The photochemical reaction gives the same product; the quantum yield using incident radiation with $\lambda = 313$ nm was $\Phi = 7 \times 10^{-4}$ mol einstein^{-1} when reaction was carried out under 1 atm of CO and $\Phi = 4 \times 10^{-3}$ mol einstein^{-1} when the reaction was carried out in the absence of free CO. Thus the photochemical reaction was also retarded by free CO.

The kinetics of reaction of CS_2 with $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ are different since the equilibrium constant for formation of the intermediate complex $[M_3(\mu_3\text{-}CO)(CS_2)(\mu\text{-dppm})_3]^{2+}$ is much lower than for SCN$^-$. Hence the major species in solution under the conditions of the kinetics were $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ and CS_2, with very little $[M_3(\mu_3\text{-}CO)(CS_2)(\mu\text{-dppm})_3]^{2+}$. Using excess CS_2, the reactions followed first-order kinetics and the observed first-order rate constants were proportional to the concentration of CS_2 (Figure 4, Table IV).[21] Thus, as expected under these conditions, the reactions followed overall second-order kinetics (Figure 4, first order in each reagent) and the second-order rate constants were 3.55×10^{-2} L mol^{-1} s^{-1} and 6.8×10^{-3} L mol^{-1} s^{-1} when M = Pt and Pd, respectively.[21] In this case, the platinum complex reacts ~5 times faster than the palladium complex. The palladium reaction did not give a product analogous to **3c**, but a complex tentatively identified as $[Pd_3(CS_2)(\mu\text{-dppm})_3]^{2+}$ (**5**) by its FAB-MS and NMR properties. However, since it is not fully characterized, the kinetic data serve only as a measure of the relative rates of reaction of the Pd_3 and Pt_3 clusters. Both reactions were retarded in the presence of free CO,[21,22] but the detailed dependence was not studied.

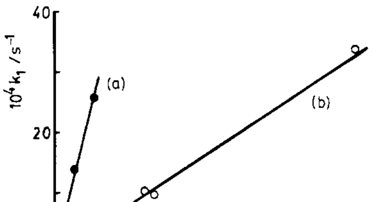
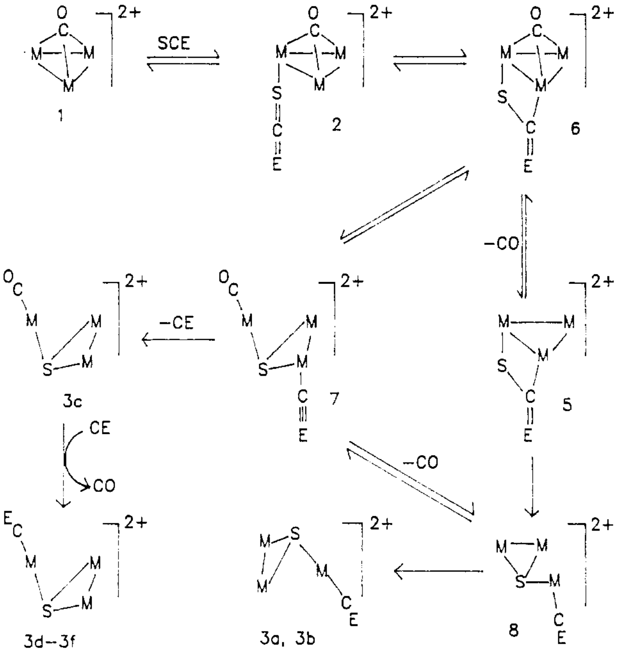


Figure 4. Graph of 10^4k_1 (s^{-1}), where k_1 is the observed first-order rate constant for reaction of $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ with CS_2 in methanol at 25 °C, vs the concentration of CS_2: (a) M = Pt; (b) M = Pd.

Scheme II



Discussion

This work has shown that C=S bond cleavage by oxidative addition to Pt_3 clusters is a general reaction and operates for all reagents SCN$^-$, RNCS, CS_2, and COS. As

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[21] When M = Pt, the plot of k_{obs} vs $[CS_2]$ is linear but does not pass through the origin. The intercept at $[CS_2] = 0$ was $k_{obs} = 1.65 \times 10^{-4}$ s^{-1}. This reaction was retarded by free CO but, because of the complicating factor outlined below,[22] a detailed study has not been attempted.

[22] For the CS_2 reaction, some retardation by CO may also be caused by reversible reaction of **1** with CO to give $[Pt_3(CO)_2(\mu\text{-dppm})_3]^{2+}$, thus inhibiting formation of intermediate **2**.[20] The mechanisms shown in Scheme II would follow the general rate law $d[3]/dt = a/(b + c[CO])$, where a, b, and c are functions of the individual rate constants. This is consistent with the observed kinetics, but Scheme II is sufficiently complex that individual rate constants cannot be determined. Hence, a more detailed study of the kinetics was not justified.

with most cluster reactions, it is difficult to determine the detailed mechanism of reaction, but this work indicates that at least two mechanisms operate and these will be discussed below.

The best defined mechanism is that which is dominant for the reagents RNCS and COS with the platinum cluster $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$. A reasonable reaction sequence is shown in Scheme II. The easy, reversible formation of the fluxional complexes **2** was established by NMR studies, and the next detectable intermediate was **3c**. A route involving the nonobservable intermediates **6** and **7** is proposed by analogy with the mechanism of Scheme I,[1-8] and we note that structure **6** is closely related to the proposed structure of the palladium complex **5**.[23] Complex **5** would be formed by dissociation of CO from **6** (Scheme II). All precedents suggest that a η^2-C,S bonded complex should be formed prior to CS bond cleavage.[1-8] When C≡E is CO or C≡NR, dissociation of CE from **7** gives **3c**, and, when C≡E is C≡NR, subsequent ligand substitution of RNC for CO gives **3d–f**. This step is expected since CO is a poor ligand for cationic platinum(II) centers.

Now, if CE does not readily dissociate from **7** (the case when CE = CN^- or CS), then CO dissociation could occur instead to give **8**. Alternatively, CO dissociation could occur from **6** to give **5** and then **8** (Scheme II). Sulfur inversion, which is well-established in complexes of this type,[9,12,16] would then give **3a** or **3b** without the intermediacy of **3c**. This mechanism is fully consistent with the kinetic data obtained for the reactions with SCN^- and CS_2. Inhibition by CO is explained by the reversible transformation of **7** to **8** (or **6** to **5**) and free CO,[22] though, in view of the complexity of Scheme II and the limited kinetic data, a quantitative interpretation is not possible. The observation that the reaction of $[Pd_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ to give $[Pd_3(\mu_3\text{-}S)CN(\mu\text{-dppm})_3]^+$ occurs *less* rapidly in more polar solvents is also inconsistent with a mechanism involving dissociation of the polar cyanide ion at an intermediate stage.

The precise structures of the proposed intermediates **6**, **7**, and **8** are of course speculative, but this work does provide an overview of how the strong C═S bond can be cleaved under mild conditions by Pt_3 clusters. The differences in the chemistry observed for reactions of heterocumulenes with the 42e clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ and $[Pt_3(\mu\text{-}CO)_3L_3]$[6,7] probably result mostly from the presence or absence, respectively, of the strongly bonded μ-dppm ligands, which are able to prevent fragmentation to binuclear and mononuclear complexes. Hence, a clearer (though still incomplete) picture of the course of the reactions can be obtained.

Experimental Section

IR spectra were recorded as Nujol mulls by using a Bruker IR/32 FTIR spectrometer. NMR spectra were recorded by using a Varian XL200 (^1H) or XL300 (^{13}C, ^{31}P and ^{195}Pt) spectrometer, using references Me_4Si (^1H, ^{13}C), H_3PO_4 (^{31}P), and aqueous K_2PtCl_4 (^{195}Pt). Kinetic studies were carried out by using a Cary 2290 spectrometer equipped with a thermostated cell compartment. Quantum yields were determined by using a PTI quantacount, calibrated by using ferrioxalate actinometry. Relative quantum yields were also checked with the PTI quantacount. The complexes $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3](PF_6)_2$ (M = Pd or Pt) and the thiocyanate adduct $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3(SCN)]PF_6$ were prepared as described previously.[9,24]

$[Pd_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]PF_6$. To a solution of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3](PF_6)_2$ (0.249 g) in acetone (20 mL) at 0 °C was added a solution of KSCN (0.56 g) in acetone (10 mL). The resulting solution was added to a solution of NH_4PF_6 (0.63 g) in H_2O (25 mL) at 0 °C, the volume was reduced under vacuum, and the brown precipitate of the *product* was isolated: yield 0.12 g; mp 180 °C dec. Anal. Calcd for $C_{77}H_{66}F_6NOP_7Pd_3S$: C, 54.3; H, 3.9; N, 0.8. Found: C, 54.6; H, 3.9; N, 1.0. IR: 2080 cm^{-1} [ν(SCN)]; 1831 cm^{-1} [ν(CO)]. FAB MS: found, *m/e* 1530, 1504; calcd for $[Pd_3(SCN)(\mu\text{-dppm})_3]^+$ 1530, $[Pd_3S(\mu\text{-dppm})_3]^+$ 1504. NMR in acetone-d_6: ^1H, δ = 4.78 [m, 3 H, $^2J(H^aH^b)$ = 14 Hz, $CH^aH^bP_2$], 5.08 [*m*, 3H, $CH^aH^bP_2$]. UV–vis: λ_{max} (CH_3OH) = 472 nm ($\epsilon = 21.9 \times 10^3$ L mol^{-1} cm^{-1}).

$[Pt_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]PF_6$. A solution of $[Pt_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]PF_6$ (0.12 g) in CH_3OH (40 mL) was irradiated for 27 h by using a medium-pressure Hg lamp and a Pyrex water filter. The product was obtained as a yellow solid by evaporation of the solution: yield 0.08 g; mp 250 °C dec. Anal. Calcd for $C_{76}H_{66}F_6NP_7Pt_3S$: C, 47.0; H, 3.4; N, 0.7. Found: C, 46.5; H, 3.7; N, 0.6. IR: 2132 cm^{-1} [ν(CN)]. NMR in acetone-d_6: ^1H, δ = 5.64 and 4.18 [*m*, CH_2P_2].

$[Pt_3(\mu_3\text{-}S)(PhNC)(\mu\text{-dppm})_3](PF_6)_2$. To a solution of $[Pt_3(\mu_3\text{-}CO)(PhNC)(\mu\text{-dppm})_3](PF_6)_2$ (0.025 g) in acetone (20 mL) was added an equimolar amount of PhNCS. The solution was stirred at room temperature for 1 h, and the *product* was isolated by evaporation of the solvent under vacuum and purified by precipitation using *n*-pentane: yield 97%; mp 265 °C dec. Anal. Calcd for $C_{82}H_{71}F_{12}NP_8Pt_3S$: C, 45.5; H, 3.3; N, 0.6. Found: C, 45.8; H, 3.5; N, 0.6. IR: 2187 cm^{-1} [ν(C≡N)].

Similarly was prepared $[Pt_3(\mu_3\text{-}S)(t\text{-BuNC})(\mu\text{-dppm})_3](PF_6)_2$ by using *t*-BuNCS: yield 95%; mp 180–183 °C. Anal. Calcd for $C_{80}H_{75}F_{12}NP_8Pt_3S$: C, 44.8; H, 3.5; N, 0.7. Found: C, 45.0; H, 3.7; N, 0.6%. IR: 2215 cm^{-1} [ν(C≡N)]. $[Pt_3(\mu_3\text{-}S)(MeNC)(\mu\text{-dppm})_3](PF_6)_2$ by using MeNCS: yield 97%; mp 208–210 °C. Anal. Calcd for $C_{77}H_{69}F_{12}NP_8Pt_3S$: C, 44.0; H, 3.3; N, 0.7. Found: C, 44.4; H, 3.4; N, 0.7. IR: 2249 cm^{-1} [ν(C≡N)]. In each case, the reaction was complete in 24 h at room temperature.

Similarly was prepared $[Pt_3(\mu_3\text{-}S)(CS)(\mu\text{-dppm})_3](PF_6)_2$ by using freshly distilled CS_2: yield 75%; mp 180 °C dec. Anal. Calcd for $C_{76}H_{66}F_{12}P_8Pt_3S_2$: C, 43.4; H, 3.2. Found: C, 43.4; H, 3.1. The reaction time was 5 h. If the reaction time was 17 h, a different, unidentified complex was formed.

Kinetic Studies. The rate of reaction of $[Pd_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]PF_6$ to give CO and $[Pd_3(\mu_3\text{-}S)(CN)(\mu\text{-dppm})_3]PF_6$ was monitored at λ = 472 nm. Computer treatment of the absorbance vs time values established that good first-order kinetics were followed for at least 4 half-lives. The concentration used was $\sim 2 \times 10^{-4}$ M. Reactions under CO atmosphere were carried out by using a 1-cm quartz cell fitted with a side-arm and a Teflon stopcock. The solvent acetone was degassed by several freeze–pump–thaw cycles, the desired pressure of CO was then added followed by nitrogen gas to give a total pressure of 1 atm. The stopcock was closed, the palladium complex and solvent were mixed and the reaction was monitored as before.

The corresponding reaction of $[Pt_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3](PF_6)$ was monitored at λ = 296 nm, and the corresponding reactions of $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3](PF_6)_2$ with CS_2 were monitored in a similar way, using a large excess of CS_2 so as to give first-order kinetics.

Acknowledgment. We thank NSERC (Canada) for financial support.

Registry No. **1**·$2PF_6^-$, 99642-80-5; **2a**·PF_6^-, 104438-45-1; **2b**·$2PF_6^-$, 122114-78-7; **2c**·$2PF_6^-$, 122114-80-1; **2d**·$2PF_6^-$, 122114-82-3; **2e**·$2PF_6^-$, 122114-84-5; **2f**·$2PF_6^-$, 122114-86-7; **3a**·PF_6^-, 122114-72-1; **3b**·$2PF_6^-$, 122114-70-9; **3b***·$2PF_6^-$, 122114-74-3; **3c**·$2PF_6^-$, 122114-68-5; **3c***·$2PF_6^-$, 122114-76-5; **3d**·$2PF_6^-$, 122114-66-3; **3e**·$2PF_6^-$, 122114-64-1; **3f**·$2PF_6^-$, 122114-62-9; **5**·$2PF_6^-$, 122114-90-3; $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3](PF_6)_2$, 89189-82-2; $[Pd_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]PF_6$, 122114-88-9; KSCN, 333-20-0; *t*-BuNCS, 590-42-1; PhNCS, 103-22-0; MeNCS, 556-61-6; CS_2, 75-15-0.

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[23] A reviewer suggests that the route may involve the longer sequence **6** → **5** → **8** → **7** → **3c** → **3d–f** (Scheme II), but this is not favored since **8** → **3d–f** would be rapid and the CO concentration low. It is, however, consistent with the CO retardation.

[24] Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344.