^{1}H NMR ($CDCl_3$): δ 4.7 (t, 1, H), 3.65 (s, 3, OCH_3), 1.57–2.17 (m, 15, CH_3, CH_2). IR (neat): 1695 cm^{-1}.

This material was not further purified.

Reaction of Vinyl-Substituted Azirines 4b–d with Chromium Carbene Complexes. These reactions were run in the usual manner, using 1 mmol of the azirine[10] and 1 mmol of the methoxymethylcarbene complex. Oxidation of the crude material followed by purification by radial layer chromatography gave **6** (50 mg, 31%), **7** (61 mg, 28%), or **8** (124 mg, 57%), respectively. Infrared, NMR, and mass spectra as well as melting points were identical with those reported for these compounds.[10]

Acknowledgment. Support for this research under Grant No. 2RO1GM21178-06 from the National Institutes of General Medical Sciences (PHS) is gratefully acknowledged. C. Y. thanks the Chendgu Institute of Organic Chemistry, Peoples Republic of China, for financial support. A. K. acknowledges the Schweizerische Nationalfonds zur Foerderung der wissenschlaftichen Forschung for partial financial support.

Registry No. **1a**, 20540-69-6; **1b**, 27436-93-7; **2a**, 14491-02-2; **2b**, 16205-14-4; **2c**, 16483-98-0; **3a**, 97704-60-4; **3a** dimer, 97719-87-4; **3b**, 97704-61-5; **3c**, 97704-62-6; **3d**, 97704-63-7; **3e**, 97704-64-8; **4b**, 42970-55-8; **4c**, 52179-65-4; **4d**, 90382-67-5; **6**, 1006-65-1; **7**, 4492-01-7; **8**, 838-40-4; **9**, 97704-65-9; **10**, 97719-88-5; benzonitrile, 100-47-0; 2-methoxy-3-methylbut-2-ene, 26578-81-4; isobutyrophenone, 611-70-1.

Reactivity and Ligand Exchange in Triplatinum Clusters

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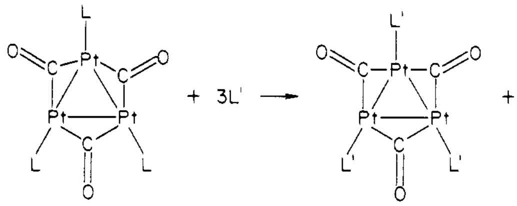
The phosphine ligands, L, in the triplatinum clusters $Pt_3(CO)_3L_3$ have been found to undergo a facile ligand substitution reaction with 3 equiv of L′ to give $Pt_3(CO)_3L'_3$ where L = P-*t*-Bu_3 and L′ = P-*t*-Bu_2Ph, L = P-*t*-Bu_2Ph and L′ = P-*t*-$BuPh_2$, PCy_3, and P-*i*-Pr_3, and L = PCy_3 and L′ = P-*i*-Pr_3. The substitution occurs by an associative mechanism with the Pt_3 triangle remaining intact during the process. Mixtures of $Pt_3(CO)_3$(P-*t*-Bu_2Ph$)_3$, **1**, and either $Pt_3(^{13}CO)_3$(P-*t*-Bu_2Ph$)_3$ or $Pt_3(CO)_3(PCy_3)_3$, **2**, scramble both phosphine and carbonyl ligands in a much slower reaction (approximately 1 h at 25 °C whereas L′ substitution occurs in about 25 s). Reactions of the cluster **1** with CS_2, OCS, and SO_2 also have been examined. In all cases, fragmentation of the trimer occurs to give dimeric products. The reaction of **1** and CS_2 results in formation of either $Pt_2(\mu\text{-}CS_2)_2$(P-*t*-Bu_2Ph$)_2$ or $Pt_2(\mu\text{-}S)(CO)_2$(P-*t*-Bu_2Ph$)_2$, **4**, depending on reaction conditions, whereas **4** is obtained from the reaction of **1** with OCS. Treatment of **1** with SO_2 at 25 °C gives $Pt_2(\mu\text{-}SO_2)(CO)_2$(P-*t*-$Bu_2Ph)_2$, **5**, which on prolonged standing in solution at 25 °C converts to the triplatinum cluster $Pt_3(CO)_2(SO_2)$(P-*t*-Bu_2Ph$)_3$, **6**. ^{31}P NMR spectroscopy reveals that the initial reaction gives mixtures of **5**, **6**, and $Pt_3(SO_2)_2(CO)$(P-*t*-Bu_2Ph$)_3$.

Introduction

The reactivity of transition-metal cluster compounds is an area of continuing interest in organometallic chemistry.[1,2] An understanding of the reactions that such systems undergo is essential for any evaluation of their potential as catalysts. We have been studying the chemistry of the triplatinum cluster $Pt_3(\mu\text{-}CO)_3L_3$, where L is a bulky phosphine ligand. While a number of these clusters have been synthesized[3] and characterized by NMR spectroscopy[4] and X-ray crystallography,[5] very little has been reported about their reactivity.

In 1970 Chatt and Chini reported[6] the synthesis of the clusters $Pt_3(CO)_3L_4$, L = PPh_3, PPh_2Me, and PPh_2Et, and $Pt_3(CO)_3L_3$, L = $PPh_2(CH_2Ph)$, by the decomposition of the mononuclear carbonyl compounds $Pt(CO)_2L_2$. They noted that the addition of free phosphine to the trinuclear clusters immediately generates monomeric species which led them to assume a possible equilibrium between $Pt_3(CO)_3L_4$ and $Pt_3(CO)_3L_3$ plus L, followed by cluster breakdown. This equilibrium has been confirmed by ^{31}P NMR studies.[4b] Shortly thereafter the analogous palladium cluster, $Pd_3(CO)_3(PPh_3)_4$ was reported.[7] This cluster reacts with an excess of PPh_3 to give $Pd(CO)(PPh_3)_3$, and it also loses a PPh_3 ligand when recrystallized from toluene resulting in formation of the compound $Pd_3(CO)_3(PPh_3)_3$.

Scheme I



L = P-*t*-Bu_3, L′ = P-*t*-Bu_2Ph
L = P-*t*-Bu_2Ph, L′ = P-*t*-$BuPh_2$, PCy_3, P-*i*-Pr_3
L = PCy_3, L′ = P-*i*-Pr_3

Recent work by Briant, Evans and Mingos has shown that the cluster $Pt_3(CO)_3(PPh_3)_4$ reacts with SO_2 to produce the SO_2-substituted compound $Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3$.[8] This is one of a small number of clusters containing the SO_2 ligand although the coordination chemistry of SO_2 has been widely studied.[9] Goel and Goel reported the cluster

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breakdown of $Pt_3(CO)_3(P\text{-}t\text{-}Bu_3)^3$ by I_2 to give the dinuclear species $Pt_2(\mu\text{-}I)_2(CO)_2(P\text{-}t\text{-}Bu_3)_2$.[10] There is also an interesting reaction between $Pt_3(CO)_3(PPh\text{-}i\text{-}Pr_2)_3$ and metallic mercury giving $[Pt_3Hg(CO)_3(PPh\text{-}i\text{-}Pr_2)_3]_2$ which consists of two triangular Pt_3 units, each capped by a mercury atom, and the tetrahedra are joined through a Hg–Hg bond.[11]

We have investigated some of the reactions that triplatinum clusters containing bulky phosphine ligands undergo, with the object of determining the stability of the triangular metal framework to fragmentation in the presence of free ligands. This paper deals with ligand substitution and scrambling reactions of these clusters and with the reactions of $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$ with small, sulfur-containing, molecules such as CS_2, OCS, and SO_2.

Results and Discussion

(a) Ligand Substitution and Scrambling Reactions. The phosphine ligands, L, in the triplatinum clusters $Pt_3(CO)_3L_3$ have been found to be labile to substitution in hexanes solution at 23 °C. The results are summarized in Scheme I.

Typical reactions required approximately 25 s for completion, and yields of the substituted trimeric compounds were quantitative. The principal requirement for the substitution to proceed appears to be that the incoming phosphine ligand, L′, be sterically less demanding than L. Implicit in the results is that the reverse reactions do not occur to a measurable extent. All products have been unambiguously characterized by IR and ^{31}P NMR spectroscopy.[4,12,13]

The reaction of $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$, **1**, with PCy_3 has been examined in somewhat greater detail than the others. While a complete kinetic study has not been undertaken, certain observations allow us to speculate about possible reaction pathways. If immediately upon addition of 3 equiv of PCy_3 to **1** a comparative TLC plate is developed, the presence of one major intermediate can be detected together with a very small amount of a second intermediate. This major intermediate can be prepared in higher yields if only 1 equiv of PCy_3 is added to solutions of **1**. Purification of the compound followed immediately by ^{31}P NMR analysis revealed it to be the mixed-phosphine trimeric cluster $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_2(PCy_3)$. This mixed-phosphine complex was observed to slowly scramble the phosphine ligands in solution generating mixtures of **1**, $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_2(PCy_3)$, and $Pt_3(CO)_3(PCy_3)_3$, **2**. A similar mixture is obtained by dissolving **1** and **2** (rigorously purified to remove any free phosphine ligands) together in hexanes. The solutions required approximately 1 h to reach constant composition. If **1** and isotopically labeled $Pt_3(^{13}CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$ are stirred together in hexanes, the carbon monoxide ligands scramble on the same time scale.

Possible mechanisms by which the phosphine substitution reactions could occur can be broadly classified into a phosphine associative process, or a phosphine dissociative process where the Pt triangle remains intact. Alternately, a mechanism involving cluster fragmentation and phosphine substitution of the mononuclear intermediates followed by reaggregation could be occurring. It seems reasonable to assume that the scrambling of both carbon monoxide and phosphine ligands, which occurs in the absence of free ligands on a slower time scale, involves fragmentation of the clusters into smaller units followed by recombination. A mechanism where two of the triangular clusters associate to form a weakly bound hexanuclear complex which then reverts to two trimers could scramble the ligands. This path is deemed less favorable due to the bulky nature of the phosphine ligands and the known tendency of Pt_3 clusters to fragment.[6]

The ligand scrambling process occurs at a much slower rate than the rate at which the phosphine substitution reaction proceeds. This observation eliminates the possibility that the substitution reaction involves initial phosphine dissociation, as that would scramble the phosphine ligands in less than 1 min. Thus the two basic possibilities for the ligand substitution pathway are an associative mechanism where the triangle of platinum atoms remains intact or another fragmentation mechanism which is accelerated by the presence of free phosphine ligand. The rate of the substitution reaction is dependent on the phosphine ligand concentration.

When an equimolar mixture of **1** and $Pt_3(^{13}CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$ is treated with 3 equiv of PCy_3 per Pt atom the only products formed after 30 s are **2** and $Pt_3(^{13}CO)_3(PCy_3)_3$. The scrambling of ^{13}CO ligands begins after the solution has stood for several minutes. This observation is only consistent with the Pt_3 triangle remaining intact during the substitution reaction. A possible reaction pathway which is in accord with our results is

$$Pt_3(CO)_3L_3 + L' \rightarrow [Pt_3(CO)_3L_3L'] \rightarrow Pt_3(CO)_3L_2L' + L$$

The stepwise substitution of the phosphine ligands ultimately would give the $Pt_3(CO)_3L'_3$ products. A cluster $Pt_3(CO)_3(PCy_3)_4$, which is similar to the proposed intermediate, has been structurally characterized.[14] Yoshida and Otsuka have shown that the mononuclear Pt complexes containing bulky phosphine ligands also substitute by an associative mechanism.[12]

Interestingly, the trinuclear cluster **1** does not give any detectable amount of a monomeric complex in the presence of a large excess of PCy_3 (300 equiv for 3 h). This is in contrast to the results found for the triplatinum clusters containing less bulky phosphine ligands, such as PPh_3, which immediately fragment to monomeric species.[6] Thus the larger phosphine ligands stabilize the trinuclear clusters relative to the mononuclear complexes.

Having demonstrated that the triangle of platinum atoms in these clusters remains intact during substitution reactions involving the terminal phosphine ligands, we began investigating reactions with ligands which prefer to bridge or add across metal–metal bonds. The reactions of the triplatinum clusters with CS_2 were examined as the CS_2 ligand is known to bridge[15] and to insert across metal–metal bonds.[16] In addition we studied the reactions of the clusters,[1] and SO_2 as the ligand is known to substitute the CO ligands in $Pt_3(CO)_3(PPh_3)_4$.[8] In all cases we were again interested in the stability of the clusters toward fragmentation into monomeric or dimeric products.

(b) Reactions of $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$, 1. (i) CS_2. While the cluster **1** is stable to fragmentation into smaller units in the presence of a large excess of phosphine ligand, it does react quickly with an excess of CS_2 to give com-

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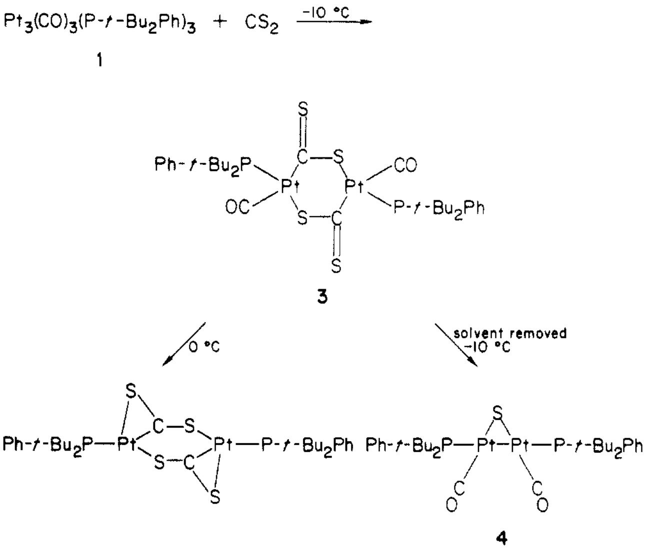
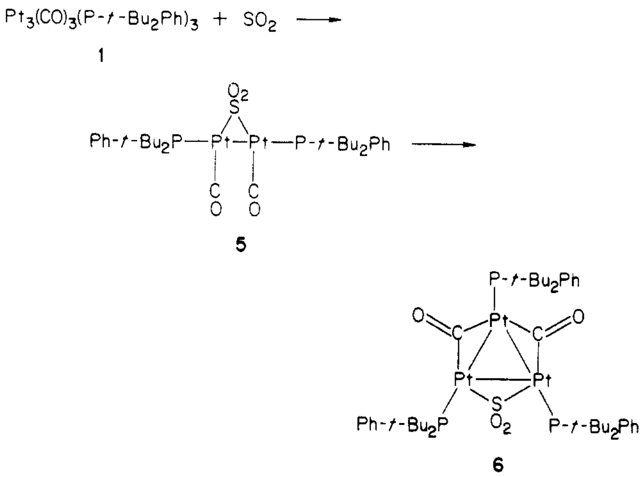
Scheme II



plexes of lower nuclearity. This reaction ultimately gives quantitative yields of the doubly CS$_2$-bridged dinuclear complex Pt$_2$(CS$_2$)$_2$(P-*t*-Bu$_2$Ph)$_2$.[17] The preliminary results of the course of the reaction of 1 with CS$_2$, monitored by variable-temperature ^{31}P NMR spectroscopy, have been previously reported.[17] At −25 °C traces of another species (δ(^{31}P) 62.2; ^1J(^{31}P–^{195}Pt) = 2600 Hz) begin to appear. The low concentration of this species makes unambiguous assignment of nuclearity difficult. While the position of the resonance and the value of ^1J(^{31}P–^{195}Pt) suggest that the intermediate is dinuclear, computer enhancement of the ^{195}Pt satellites does not reveal any evidence of coupling to a distant Pt spin. Increasing the temperature to −10 °C gives complete conversion to a second dinuclear intermediate described previously.[17] The ^{31}P NMR spectrum of this intermediate 3 reveals the presence of two chemically equivalent P environments and an IR spectrum of the complex has bands which are assigned to terminal CO and bridging CS$_2$ groups at 2019 and 975 cm^{-1}, respectively. The product Pt$_2$(CS$_2$)$_2$(P-*t*-Bu$_2$Ph)$_2$ forms at 0 °C also previously reported.[17] These results are summarized in Scheme II. The ν(CS$_2$) vibration of the intermediate 3 agrees with that reported for the related complex Pt$_2$Cl$_2$(μ-CS$_2$)(Ph$_2$PCH$_2$PPh$_2$).[15] Attempts to isolate this complex by removing the solvent while the temperature is maintained at −10 °C resulted in formation of Pt$_2$(μ-S)(CO)$_2$(P-*t*-Bu$_2$Ph)$_2$ (4). Complex 4 has been characterized by IR and ^{31}P NMR spectroscopy and elemental analysis. A similar complex, Pt$_2$(μ-S)(CO)(PPh$_3$)$_3$, has been studied by X-ray crystallography[18] and ^{31}P NMR spectroscopy.[19] The trans phosphine geometry is assigned on the basis of the large ^{31}P–^{31}P coupling constant of 129 Hz. A value of 179.8 Hz is reported for the related coupling in the complex Pt$_2$(μ-S)(CO)(PPh$_3$)$_3$ with the cis coupling being 21.5 Hz.[19] Balch et al. in analyzing the ^{31}P NMR spectrum of Pt$_2$(μ-S)(CO)(PPh$_3$)$_3$ and similar complexes have demonstrated that the Pt satellite resonances can be used to unambiguously assign the dinuclear structure.[17] Fragmentation of coordinated CS$_2$ in a dinuclear Pt complex resulting in the sulfido-bridged compound Pt$_2$(μ-S)(CS)(PPh$_3$)(Ph$_2$P(CH$_2$)$_2$PPh$_2$) has recently been reported.[16]

Scheme III



Thus the triplatinum cluster 1 fragments in the presence of excess CS$_2$ at low temperatures. We have shown that the doubly CS$_2$-bridged dinuclear complexes Pt$_2$(CS$_2$)$_2$L$_2$, where L is a bulky phosphine ligand, can be prepared quantitatively from the reaction of PtL$_2$ with CS$_2$[17] and that this reaction probably involves Pt(η^2-CS$_2$)L$_2$ as an intermediate.[20] The reaction of 1 with CS$_2$ likely has a similar type of monomeric intermediate which then dimerizes to give 3. As the temperature increases, the μ-CS$_2$ ligand in 3 becomes π-bound to a Pt atom as the CO ligand is displaced resulting in the observed product.

Facile cleavage of the CS$_2$ ligand by 1 resulting in the μ-S complex 4 is not a unique reaction. The OCS ligand reacts with 1 at 23 °C to give 4. The reaction with OCS is quantitative and can be viewed in a similar manner to that with CS$_2$. Cleavage of the η^2OCS ligand in monomeric Pt complexes is known, and this is the method by which the analogue of 4, Pt$_2$(μ-S)(CO)(PPh$_3$)$_3$, was formed.[18]

(ii) SO$_2$. The initial product which is isolated from the reaction of 1 and SO$_2$ is the dinuclear platinum complex Pt$_2$(μ-SO$_2$)(CO)$_2$(P-*t*-Bu$_2$Ph)$_2$, 5, in 75% yield as the hexane-insoluble fraction. Complex 5 has been characterized by IR (ν(C=O) and ν(SO$_2$) vibrations), ^{31}P NMR spectroscopy, and elemental analysis. The ^{31}P Pt satellites indicate a dinuclear complex and the ^3J(Pt–P) value is consistent with a trans structure. Solutions of 5 convert slowly at 25 °C to the triplatinum cluster Pt$_3$(CO)$_2$(SO$_2$)(P-*t*-Bu$_2$Ph)$_3$, 6. Again the nuclearity and symmetry of the cluster is evident in the ^{31}P NMR spectrum, vibrations associated with bridging CO and SO$_2$ ligands are observed in the IR spectrum and analytical data has been obtained. This sequence is summarized in Scheme III.

The ^{31}P NMR spectrum of a toluene solution of the reaction of 1 and SO$_2$ at 25 °C after 30 min indicates the presence of 5 (85%), 6 (10%), and Pt$_3$(CO)(SO$_2$)$_2$(P-*t*-Bu$_2$Ph)$_3$, 7 (5%). The nuclearity and symmetry of the clusters 6 and 7 are apparent in the ^{31}P NMR with two distinct phosphorus environments resulting in a doublet–triplet center-band spectrum with appropriate Pt satellites reminiscent of that observed for Pt$_3$(CO)$_3$(P-*t*-Bu$_2$Ph)$_2$(PCy$_3$). Analytically pure samples of 7 could not be obtained. However, the complex has been completely characterized by using spectroscopic data. Heating the solution to 60 °C results in complete conversion to 6. Under an atmosphere of CO both 6 or a mixture of 6 and 7 convert back to the SO$_2$-bridged dimer 5, together with

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a small amount of Pt metal and OP-*t*-Bu_2Ph. The triplatinum clusters 1 or $Pt_3(SO_2)_3(P\text{-}t\text{-}Bu_2Ph)_3$[22] were not observed during these interconversions, nor did we detect any mononuclear species.

Moody and Ryan[21] have structurally characterized the triplatinum cluster $Pt_3(SO_2)_3(PPh_3)_3$, which was prepared by slow removal of SO_2 from a toluene solution of $Pt(SO_2)_2(PPh_3)_2$. An intermediate in this reaction was isolated. However, due to its instability it was not completely characterized. Analytical data given[21] for this intermediate are consistent with the formula $Pt_2(SO_2)(PPh_3)_4$, and the complex may be the tetrakis(phosphine) analogue of **5**. We have not been able to detect any monomeric complexes in the reaction of **1** and SO_2. As observed in the previous sections, the platinum carbonyl complexes with bulky phosphine ligands seem to favor dimeric or trimeric structures.

The facile interconversion of these complexes suggests that the fragmentation and aggregation reactions are low energy processes. It also appears that the bridging CO and SO_2 ligands have comparable bond strengths. It is interesting that the reaction of $Pt_3(CO)_3(PPh_3)_4$ with SO_2 at 60 °C gives $Pt_3(SO_2)_3(PPh_3)_3$[8] while reaction of **1** results in the mixed CO,SO_2 trimers **6** and **7**. This may reflect the greater σ-donor ability of P-*t*-Bu_2Ph, with respect to PPh_3, and thus total replacement of CO with the weaker π-acid ligand SO_2 is not favored in **1**. We are undertaking a kinetic study to elucidate the details of the reaction of **1** and SO_2.

Summary

The triplatinum clusters $Pt_3(CO)_3L_3$, where L is a bulky phosphine ligand such as P-*t*-Bu_2Ph, undergo rapid phosphine substitution by a pathway in which the metal triangle remains intact. There are no detectable amounts of monomeric Pt complexes formed even after the addition of a large excess (300 equiv) of phosphine ligand. This is in contrast to the triplatinum clusters with smaller phosphine ligands, such as PPh_3, which fragment to monomeric complexes $Pt(CO)L_3$ immediately upon addition of excess phosphine.[6] The presence of low concentrations of mononuclear species in the bulky phosphine trimer solutions is suggested by the ligand scrambling experiments in which both CO and L ligands are exchanged at 25 °C in a much slower process than that observed for substitution. This increased stability of the trimers to fragmentation is ascribed to steric effects from the bulkier phosphine ligands. This stability appears to be restricted to terminal two-electron donor ligands, such as phosphine, as we have observed fragmentation on reaction with ligands which prefer to bridge metal–metal bonds.

The cluster **1** fragments immediately when reacted with small molecules such as CS_2, OCS, and SO_2. These reactions occur under mild conditions for example with CS_2 the reaction begins at −25 °C and appears to proceed via a monomeric complex which then dimerizes. The OCS ligand gives a diplatinum product and SO_2 initially forms $Pt_2(SO_2)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_2$, **5**, which converts to triplatinum clusters. The ease with which these complexes interconvert and the fact that changes in the ligands prompt this fragmentation or aggregation suggests that the Pt–Pt interactions in these clusters are relatively weak.

Experimental Section

All reactions were performed under an N_2 atmosphere, and the solvents were dried and distilled prior to use. The phosphines were purchased from Strem Chemicals Inc. with the exception of P-*t*-Bu_2Ph and P-*t*-Bu_3 which were prepared by literature methods.[23-25] The cluster $Pt_3(CO)_3L_3$ (L = P-*t*-Bu_2Ph and P-*t*-Bu_3) were also synthesized by literature methods.[12]

Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. The ^{13}C and ^{31}P NMR spectra were recorded by using a Varian XL 200 Spectrometer operating at 50.3 and 81.0 MHz, respectively. The ^{13}C chemical shifts were measured relative to an internal solvent reference and then reported relative to a tetramethylsilane (Me_4Si) standard, while ^{31}P shifts were measured relative to external $P(OMe)_3$ in $CO(CD_3)_2$ and are reported relative to H_3PO_4.

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

Reaction of $Pt_3(CO)_3L_3$ with 3 Equiv of L′ (L = P-*t*-Bu_3, L′ = P-*t*-Bu_2Ph; L = P-*t*-Bu_2Ph, L′ = PCy_3, P-*i*-Pr_3, P-*t*-$BuPh_2$; L = PCy_3, L′ = P-*i*-Pr_3). In all reactions 3 equiv of the appropriate phosphine L′ was added to 0.05 g of $Pt_3(CO)_3L_3$ in 25 mL of hexanes. After 5 min of stirring (23 °C) the solvent was removed at reduced pressure and the resulting red solids were washed with EtOH (30 mL). The reaction time has been measured by IR spectroscopy and comparative TLC to be approximately 25 s (±10 s). When 10 equiv of the appropriate phosphine ligand was added, the reaction time as measured by IR spectroscopy was less than 10 s. Yields are quantitative and the products $Pt_3(CO)_3L'_3$ have all been previously reported and were characterized by IR and ^{31}P NMR spectroscopy. $Pt_3(CO)_3(P\text{-}t\text{-}Bu_3)_3$: see ref 12; ^{31}P NMR (toluene at 25 °C) δ 94.0, $|^1J(^{195}Pt, ^{31}P)| = 5226$ Hz, $|^2J(^{195}Pt,^{31}P)| = 378$ Hz, $|^3J(^{31}P,^{31}P)| = 40$ Hz. $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$: see ref 12; ^{31}P NMR (toluene at 25 °C) δ 86.2 $|^1J(^{195}Pt,^{31}P)| = 5037$ Hz, $|^2J(^{195}Pt,^{31}P)| = 432$ Hz, $|^3J(^{31}P,^{31}P)| = 50$ Hz. $Pt_3(CO)_3(PCy_3)_3$ and $Pt_3(CO)_3(P\text{-}i\text{-}Pr_3)_3$: see ref 4a. $Pt_3(CO)_3(P\text{-}t\text{-}BuPh_2)_3$: see ref 13.

Reaction of $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$ (1) with 1 Equiv of PCy_3. $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$ (0.100 g, 0.075 mmol) and PCy_3 (0.020 g, 0.075 mmol) were stirred together in 25 mL of hexanes (23 °C) for 5 min. The products were isolated (as above), separated by using preparative thin-layer chromatography (TLC) (0.25 mm Merck Kieselgel 60F) eluting with 2% EtOAc in hexanes and characterized by ^{31}P NMR spectroscopy. The approximate composition was as follows: $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$, 45%, R_f 0.06; $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_2(PCy_3)$, 45%, R_f 0.13, ^{31}P NMR (CH_2Cl_2 at 25 °C) δ 56.9 (t, 50 Hz, PCy_3), 90.5 (d, 50 Hz, P-*t*-Bu_2Ph), $|^1J(^{195}Pt,^{31}P)|$ PCy_3 = 4623 Hz, P-*t*-Bu_2Ph = 4904 Hz, $|^2J(^{195}Pt,^{31}P)|$ PCy_3 = 405 Hz, P-*t*-Bu_2Ph = 465 Hz; $Pt_3(CO)_3(PCy_3)_3$, 10%, R_f 0.23.

Reaction of 1 with $Pt_3(CO)_3(PCy_3)_3$. Both **1** and $Pt_3(CO)_3(PCy_3)_3$ were rigorously purified by preparative TLC and recrystallization to remove any free phosphine ligands. **1** (0.020 g, 0.0149 mmol) and $Pt_3(CO)_3(PCy_3)_3$ (0.022 g, 0.0147 mmol) were stirred together in 40 mL of hexanes (23 °C). The reaction was monitored by comparative TLC. A constant, approximately equal mixture of **1**, $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_2(PCy_3)$, and $Pt_3(CO)_3(PCy_3)_3$ was observed after 60 min (±10 min).

Preparation of $Pt_3(^{13}CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$. The ^{13}CO isotopically labeled cluster was prepared by the method of Otsuka et al.[13] using 99% ^{13}C-enriched CO and was characterized by IR and ^{13}C NMR spectroscopy. $Pt_3(^{13}CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$: ^{13}C NMR δ 242.0 $|^1J(^{195}Pt,^{13}C)| = 763$ Hz, the sum of all ^{31}P and ^{13}C coupling constants for the AA′A″XX′X″ spin system[26] is 45 Hz; IR ν(CO) 1729 (s), 1787 (w) cm^{-1}.

Reactions of $Pt_3(^{13}CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$ with $Pt_3(CO)_3L_3$ (L = P-*t*-Bu_2Ph, PCy_3). Equal volumes of a solution of $Pt_3(^{13}CO)_3(P\text{-}t\text{-}Bu_2Ph)_3$ (7.48×10^{-4} M) or **1** and **2** (7.48×10^{-4} M) were mixed in an IR solution cell, and the spectra were recorded every 30 s for 1 h. (See Results and Discussion).

Reaction of 1 with CS_2. Variable-Temperature ^{31}P NMR Study. **1** (0.10 g) was dissolved in 3 mL of CH_2Cl_2, the temperature was reduced to −78 °C, and 4 drops of CS_2 were added. The temperature was increased in 10 °C increments, and the

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[22] Prepared by the reaction of $Pt(C_2H_4)_2(P\text{-}t\text{-}Bu_2Ph)$ and SO_2. Farrar, D. H.; Gukathasan, R. R., unpublished results.

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spectral data acquired for 45 min at each temperature. The final temperature was 28 °C.

Attempts To Isolate the Intermediate in the Reaction of 1 with CS_2. The above reaction was repeated except at −10 °C the solvents were removed under vacuum resulting in isolation of the compound $Pt_2(S)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_2$. This was crystallized from CH_2Cl_2/hexane solution: ^{31}P NMR (CH_2Cl_2 at 25 °C) δ 71.16, $|^1J(^{31}P, ^{195}Pt)| = 3173$ Hz, $|^2J(^{31}P,^{195}Pt)| = 129$ Hz, $|^3J(^{31}P,^{31}P)| = 129$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 2010 (s), 1969 (w) cm^{-1}. Anal. Calcd for $Pt_2SP_2O_2C_{30}H_{46}$: C, 39.0; H, 5.0; S, 3.5; P, 6.7. Found: C, 38.9; H, 5.0; S, 3.6; P, 6.8.

Reaction of 1 with OCS. 1 (0.100 g, 0.078 mmol) was dissolved in 10 mL of toluene, and OCS was bubbled through the solution for 5 min, followed by stirring under an atmosphere of OCS for 12 h. The volume was reduced to 1–2 mL, and hexane was added. The yellow-brown precipitate was filtered, washed with diethyl ether, and dried in air; yield 82%. It was characterized by ^{31}P NMR and IR spectroscopy as $Pt_2(S)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_2$ (**4**).

Preparation of $Pt_2(SO_2)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_2$ (5). 1 (0.10 g, 0.075 mmol) was dissolved in 10 mL of toluene. SO_2 was bubbled through it for 1 min, and the volume was then reduced to 1–2 mL. The addition of hexane under a CO atmosphere gave yellow crystals which were filtered, washed with diethyl ether, and dried in air: yield 75%; ^{31}P NMR (CH_2Cl_2 at 25 °C) δ 58.73, $|^1J(^{31}P,^{195}Pt)| = 3980$ Hz, $|^2J(^{31}P,^{195}Pt)| = 328$ Hz, $|^3J(^{31}P,^{31}P)| = 76$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 2040 (s), 2001 (w) (SO_2) cm^{-1}, 1049 (w), 1067 (m), 1180 (m) cm^{-1}. Anal. Calcd for $Pt_2S_1P_2O_4C_{30}H_{46}$: C, 37.7; H, 4.8; P, 6.5; S, 3.3. Found: C, 38.6; H, 5.1; P, 6.5; S, 3.5.

Preparation of $Pt_3(SO)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_3$ (6). **5** (0.025 g) was dissolved in 5 mL of CH_2Cl_2/hexane solution and allowed to stand for a period of 2 weeks, during which time yellow-orange crystals were formed: yield 75%; ^{31}P NMR (CH_2Cl_2 at 25 °C) δ 83.6 (d, 49 Hz), $|^1J(^{195}Pt,^{31}P)| = 4395$ Hz, $|^2J(^{195}Pt,^{31}P)| = 394$ Hz, δ 103.8 (t, 49 Hz), $|^1J(^{195}Pt,^{31}P)| = 4395$ Hz, $|^2J(^{195}Pt,^{31}P)| = 479$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 1811 (s), 1847 (s) (SO_2) cm^{-1}, 1060 (s), 1203 (m) cm^{-1}. Anal. Calcd for $Pt_3SP_3O_4C_{44}H_{69}$: C, 38.5; H, 5.0; P, 6.8; S, 2.3. Found: C, 38.3; H, 5.0; P, 6.9; S, 2.3.

Characterization of $Pt_3(CO)(SO_2)_2(P\text{-}t\text{-}Bu_2Ph)_3$ (7). Complex 1 was observed in ^{31}P NMR and IR spectra as a minor product (5%) from the reaction of 1 and SO_2 at 25 °C. We were unable to separate this complex from the mixture to obtain analytically pure samples: ^{31}P NMR (toluene at 25 °C) δ 87.7 (d, 51 Hz), $|^1J(^{195}Pt,^{31}P)| = 4476$ Hz, $|^2J(^{195}Pt,^{31}P)| = 420$ Hz, δ 64.8 (t, 56 Hz), $|^1J(^{195}Pt,^{31}P)| = 4476$ Hz, $|^2J(^{195}Pt,^{31}P)| = 327$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 1857 (s), 1730 (s) cm^{-1}.

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Registry No. 1, 62931-81-1; **2**, 62987-80-8; **3**, 97689-47-9; **4**, 97689-48-0; **5**, 97703-27-0; **6**, 97719-79-4; **7**, 97703-28-1; $Pt_3(CO)_3(P\text{-}t\text{-}Bu_3)_2(PCy_3)$, 71080-86-9; $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_2(PCy_3)$, 97689-49-1; $Pt_3(CO)_3(P\text{-}i\text{-}Pr_3)_3$, 71080-84-7; $Pt_3(CO)_3(P\text{-}t\text{-}BuPh_2)_3$, 71080-85-8; PCy_3, 2622-14-2; $P\text{-}i\text{-}Pr_3$, 6476-36-4; $P\text{-}t\text{-}Bu_2Ph$, 32673-25-9; $P\text{-}t\text{-}BuPh_2$, 6002-34-2; $Pt_2(CS_2)_2(P\text{-}t\text{-}Bu_2Ph)_2$, 91686-59-8.

Oxidative Addition of Cyclopropenyl Cations to Zerovalent Molybdenum and Tungsten Centers. Synthesis of η^3-Cyclopropenyl and η^3-Oxocyclobutenyl Complexes of Molybdenum(II) and Tungsten(II). Crystal and Molecular Structures of $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3Ph_2R)(CO)_2]$ (R = Ph, *t*-Bu)

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Oxidative addition of triphenylcyclopropenyl *hexafluorophosphate* to $[Mo(CO)_3(MeCN)_3]$ affords the cationic cyclopropenyl complex $[Mo(\eta\text{-}C_3Ph_3)(CO)_2(MeCN)_3]^+[PF_6^-]$, **8**, which reacts with cyclopentadienylthallium to give excellent yields of the neutral η^3-cyclopropenyl complex $[Mo(\eta\text{-}C_3Ph_3)(\eta\text{-}C_5H_5)(CO)_2]$, **6a**. Similar one-pot syntheses of the analogous complexes $[M(\eta\text{-}C_3Ph_2\text{-}t\text{-}Bu)(\eta\text{-}C_5H_5)(CO)_2]$ (**6b**, M = Mo; **6c**, M = W) from the *tert*-butyldiphenylcyclopropenyl cation are described. In contrast, use of triphenylcyclopropenyl *chloride* or *bromide* in the reaction with $[M(CO)_3(MeCN)_3]$ (M = Mo, W) affords ultimately the ring-expanded oxocyclobutenyl compounds **9**, presumably via intermediates **10**. Thermal reaction of the (triphenylcyclopropenyl)molybdenum complex **6a** with PMe_2Ph or $P(OPh)_3$ results in ring expansion to give the oxocyclobutenyl complexes 11. The dynamic behavior of the cyclopropenyl ligands in compounds **6** is reported, and compounds **6a** and **6b** have been characterized by single-crystal X-ray diffraction studies: **6a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.545$ (2) Å, $b = 16.580$ (3) Å, $c = 14.463$ (3) Å, $\beta = 98.47$ (2)°, and $Z = 4$; **6b** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.488$ (2) Å, $b = 16.394$ (4) Å; $c = 16.168$ (4) Å, $\beta = 95.28$ (2)°, and $Z = 4$. Both compounds clearly contain η^3-cyclopropenyl ligands, and their structures are compared and contrasted with those of other cyclopropenyl and metallacyclobutadiene complexes.

Introduction

A mechanism for transition-metal-catalyzed alkyne metathesis involving transition metal–alkylidyne and metallacyclobutadiene intermediates was proposed by Katz in 1975.[3] More recently, Schrock has synthesized a number of tungsten–alkylidyne complexes and has found that they catalyze the metathesis of alkynes,[4] with activities far

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