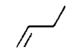
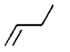
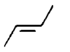
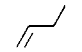
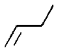
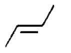
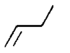
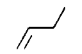
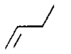
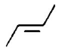
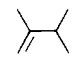
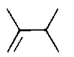
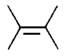
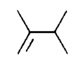
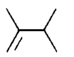
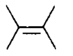
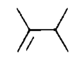
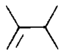
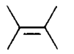
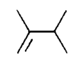
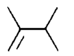
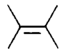
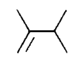
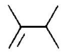
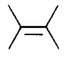
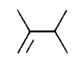
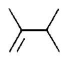
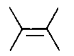
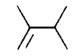
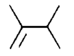
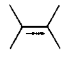
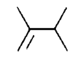
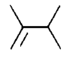
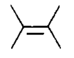
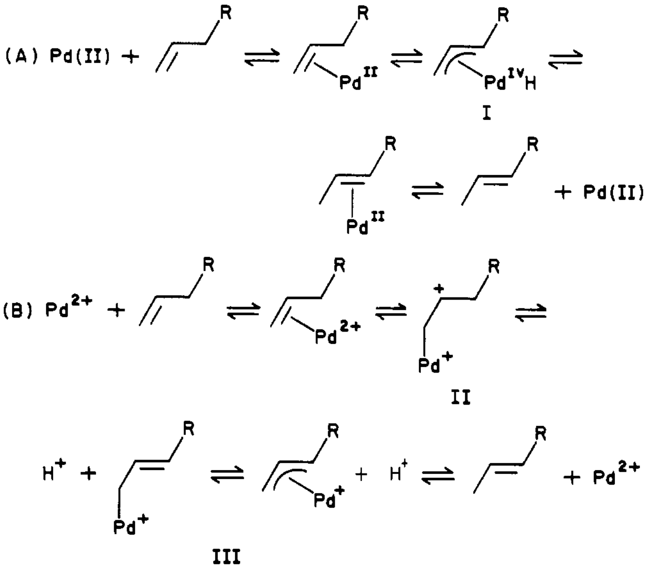
Table I

| catalyst | olefin | olefin/ catalyst | solvent | time[i] | product, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1[a] |  | *f* | $CH_3CN$ | 1 h |  | (6) |  | (66) |  | (28)[g] |
| 1[b] + $PPh_3$[d] |  | *f* | $CHCl_3$ | 10 h |  | (4) |  | (68) |  | (28)[g] |
| 1[b] + 2 $PPh_3$[d] |  | *f* | $CHCl_3$ | 10 h |  | (23) |  | (57) |  | (20)[g] |
| 1[b] + 3 $PPh_3$[d] |  | *f* | $CHCl_3$ | 1 day |  | (100) |  | (0) |  | (0)[g] |
| 1[c] |  | 10 | $CH_3CN$ | 20 min |  | (14) |  | (86)[h] | | |
| 1[c] + $PPh_3$[d] |  | 10 | $CHCl_3$ | 1.5 h |  | (12) |  | (88)[h] | | |
| 1[c] + 2 $PPh_3$[d] |  | 10 | $CHCl_3$ | 6 h |  | (80) |  | (20)[h] | | |
| 1[c] + 3 $PPh_3$[d] |  | 10 | $CHCl_3$ | 1 day |  | (100) |  | (0)[h] | | |
| 1[c] + $PPh_2Me$[d] |  | 10 | $CHCl_3$ | 3 h |  | (13) |  | (87)[h] | | |
| 1[c] + 2 $PPh_2Me$[d] |  | 10 | $CHCl_3$ | 6 h |  | (83) |  | (17)[h] | | |
| 1[c] + 3 $PPh_2Me$[d] |  | 10 | $CHCl_3$ | 12 h |  | (100) |  | (0)[h] | | |
| $Pd(PhCN)_2Cl_2$[e] |  | 10 | $CHCl_3$ | 3 h |  | (100) |  | (0)[h] | | |

[a] Concentration 1.1 × 10$^{-2}$ M. [b] Concentration 1.9 × 10$^{-2}$ M. [c] Concentration 9 × 10$^{-2}$ M. [d] 1-3 equiv of $PPh_2R$ (R = Ph, Me) was added to a solution of 1 prior to the addition of the olefin. [e] $[Pd(PhCN)_2Cl_2]$ = 1 × 10$^{-2}$ M. [f] The solution was saturated with 1-butene. [g] Thermodynamic equilibrium ratio ~6:67:27. [h] Thermodynamic equilibrium ratio ~12:88. [i] Temperature 25 °C.

**Scheme I**



**B. 2,3-Dimethyl-1-butene.** A 0.12-mL portion of 2,3-dimethyl-1-butene was added to a solution of **1** (50 mg) in $CH_3CN$ (1.2 mL) and the mixture stirred at 25 °C for 20 min. The products were analyzed by GC using a Porapak N column. Similar procedures were used in reactions in which tertiary phosphines were added to **1** prior to the addition of the olefin or when $Pd(PhCN)_2Cl_2$, $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$, or $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ was employed.

The Pd compound formed in the above reaction was $[\eta^3\text{-}(CH_2CMeCMe_2)Pd(CH_3CN)_2](BF_4)_2$. This compound was isolated as an unstable solid by the addition of anhydrous $Et_2O$ to the reaction mixture. $^1H$ NMR ($CD_3CN$): δ 3.95 (1 H, br), 3.36 (1 H, br), 2.10 (3 H, s), 1.50 (3 H, s), 1.30 (3 H, s), 1.98 (6 H, s, $CH_3CN$). IR ($CH_3CN$): $\bar{\nu}$(—C≡N), 2335 cm$^{-1}$; $\bar{\nu}(BF_4^-)$, 1100–1000 cm$^{-1}$. This compound was formed by the reaction of either 2,3-dimethyl-1-butene or 2,3-dimethyl-2-butene with **1** in $CH_3CN$ at 25 °C.

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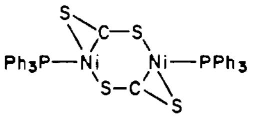
# Reaction of $CS_2$ with Trinuclear Pd and Pt Clusters. Crystal Structure of $Pt_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_2Ph)_2$

David H. Farrar,* Ravi R. Gukathasan, and Stephen A. Morris

*Received January 19, 1984*

In 1967 Baird and Wilkinson[1] synthesized $Ni_2(CS_2)_2(PPh_3)_2$ by the reaction of $Ni(CO)_2(PPh_3)_2$ and $CS_2$. This reaction was also examined by Mason, Swepston, and Ibers,[2] but all attempts to obtain single crystals suitable for X-ray analysis failed, due to poor solubility. Recently crystals of the Ni complex have been isolated,[3] and the structure was determined to be the doubly $CS_2$-bridged dimeric structure **1**.



1

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(1) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 865.
(2) Mason, M. G.; Swepston, P. N.; Ibers, J. A. *Inorg. Chem.* **1983**, *22*, 411.
(3) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Chem. Commun.* **1983**, 753.

0020-1669/84/1323-3258$01.50/0 © 1984 American Chemical Society

**Table I.** Crystal Data and Experimental Conditions Associated with Data Collection

| | |
|---|---|
| mol formula | $C_{15}H_{23}PS_2Pt$ |
| fw | 493.54 |
| system | monoclinic |
| space group | $P2_1/n$ |
| *a*, Å | 8.339 (1) |
| *b*, Å | 14.034 (1) |
| *c*, Å | 15.123 (1) |
| *β*, deg | 91.781 (9) |
| V, g cm$^{-3}$ | 1769.0 |
| *d*(calcd) | 1.85 |
| *Z* | 4 |
| *μ*(Mo Kα), cm$^{-1}$ | 83.18 |
| radiation | Mo Kα, graphite monochromatized |
| λ, Å | 0.710 73 |
| temp, °C | 26 |
| approx cryst dimens, cm | 0.030 × 0.021 × 0.016 |
| no.; 2*θ* range centrd reflcns, deg | 22; $23 < 2\theta < 33$ |
| data collcd | *hkl* and $hk\bar{l}$, for $0 < 2\theta < 50°$ |
| scan mode | *θ*–2*θ* |
| scan width, deg | 0.80 |
| max scan time, s | 75 |
| prescan rate, deg min$^{-1}$ | 11 |
| acceptance ratio, *σ*(*I*)/*I* | 0.04 |

We have found that the clusters $M_3(CO)_3L_3$ (M = Pt, L = P(*t*-Bu)$_2$Ph; M = Pd, L = P(*t*-Bu)$_2$Ph, P(*t*-Bu)$_3$) react with $CS_2$ to ultimately give complexes with similar spectroscopic properties to those reported for **1**.[3] A single-crystal X-ray diffraction study of the Pt complex revealed that these products are also isostructural with **1**. Moody et al.[4,5] have reported the related reactions of $PtL_2$ and $Pt(C_2H_4)_2L$ (L = $PCy_3$, P(*t*-Bu)$_3$) with $CS_2$. On the basis of analytical, spectroscopic, and molecular weight data, the products were formulated as trinuclear species $Pt_3(CS_2)_3L_3$. We have shown that the products are in fact the $CS_2$-bridged dimeric complexes $Pt_2(CS_2)_2L_2$.

We now report the synthesis of the doubly-$CS_2$ bridged dinuclear complexes $M_2(\mu\text{-}CS_2)_2L_2$ from $M_3(CO)_3L_3$, together with the crystal structure of $Pt_2(\mu\text{-}CS_2)_2$(P(*t*-Bu)$_2$Ph)$_2$ (**2**).

## Experimental Section

All reactions were carried out under $N_2$ atmosphere. The solvents were dried under $N_2$, and oxygen was removed by the freeze-evacuation technique. The phosphines P(*t*-Bu)$_3$ and P(*t*-Bu)$_2$Ph were prepared by treating PCl(*t*-Bu)$_2$ with appropriate organolithium reagents.[6-8] The clusters $M_3(CO)_3L_3$ (M = Pt, L = P(*t*-Bu)$_2$Ph; M = Pd, L = P(*t*-Bu)$_3$, P(*t*-Bu)$_2$Ph) were synthesized by literature methods.[9] Infrared spectra, as Nujol mulls, were recorded on a Pye Unicam SP1025 spectrometer. The $^{31}P$ NMR spectra were recorded as $CH_2Cl_2/CS_2$ solutions on a Bruker WP80 or Varian XL200 operating at 32.3 and 81 MHz, respectively. Variable-temperature NMR spectra were recorded on a Bruker WP80. The chemical shifts were measured relative to external P(OMe)$_3$ in $C_6D_6$ or $CO(CD_3)_2$.

**Preparation of Complexes. $M_2(\mu\text{-}CS_2)_2L_2$ (M = Pt, L = P(*t*-Bu)$_2$Ph (2); M = Pd, L = P(*t*-Bu)$_2$Ph, P(*t*-Bu)$_3$).** A 0.1-g portion of $M_3(CO)_3L_3$ and 2 mL of $CS_2$ were stirred together in 15 mL of hexane at 25 °C for 15 min, giving quantitative yields of $M_2(\mu\text{-}CS_2)_2L_2$. The products were isolated by filtration and recrystallized from $CH_2Cl_2/CS_2$/hexane mixtures.

**$Pd_2(CS_2)_2$(P(*t*-Bu)$_2$Ph).** Anal. Calcd for $C_{30}H_{46}P_2S_4Pd$: C, 44.50; H, 5.74. Found: C, 44.2; H, 5.6.

**$Pd_2(CS_2)_2$(P(*t*-Bu)$_3$)$_2$.** Anal. Calcd for $C_{26}H_{54}P_2S_4Pd$: C, 40.56; H, 7.09. Found: C, 40.4; H, 7.1.

**Collection and Reduction of X-ray Data.** Yellow-orange crystals of $Pt_2(\mu\text{-}CS_2)_2$(P(*t*-Bu)$_2$Ph)$_2$ were obtained by recrystallization from $CS_2$/hexane mixtures. A photographic examination showed the crystals belonged to the monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$, $C_{2h}^5$, No. 14.[10] Crystal data are presented in Table I.

**Table II.** Atomic Positional and Thermal Parameters[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Pt | 0.15403 (3) | 0.10963 (2) | 0.03916 (2) | 1.849 (4) |
| S(1) | 0.1573 (3) | 0.0621 (2) | 0.1873 (1) | 3.55 (4) |
| S(2) | −0.0665 (2) | −0.0872 (1) | 0.1039 (1) | 2.73 (3) |
| P | 0.3153 (2) | 0.2426 (1) | 0.0104 (1) | 1.99 (3) |
| C(1) | 0.0525 (8) | 0.0068 (5) | 0.1063 (4) | 2.2 (1) |
| C(11) | 0.2363 (8) | 0.3187 (5) | −0.0795 (4) | 2.2 (1) |
| C(12) | 0.0708 (8) | 0.3269 (5) | −0.0857 (5) | 3.0 (1) |
| C(13) | −0.003 (1) | 0.3910 (6) | −0.1464 (6) | 3.9 (2) |
| C(14) | 0.091 (1) | 0.4419 (6) | −0.2023 (5) | 4.5 (2) |
| C(15) | 0.253 (1) | 0.4330 (6) | −0.1994 (5) | 4.4 (2) |
| C(16) | 0.325 (1) | 0.3713 (6) | −0.1370 (6) | 3.8 (2) |
| C(21) | 0.322 (1) | 0.3289 (5) | 0.1066 (5) | 3.7 (2) |
| C(22) | 0.419 (1) | 0.2856 (7) | 0.1839 (6) | 5.6 (2) |
| C(23) | 0.151 (1) | 0.3432 (6) | 0.1347 (6) | 5.0 (2) |
| C(24) | 0.391 (1) | 0.4263 (6) | 0.0822 (6) | 5.5 (2) |
| C(31) | 0.5207 (9) | 0.2004 (6) | −0.0181 (5) | 3.4 (2) |
| C(32) | 0.572 (1) | 0.1223 (6) | 0.0469 (7) | 4.7 (2) |
| C(33) | 0.657 (1) | 0.2758 (7) | −0.0171 (8) | 5.9 (2) |
| C(34) | 0.502 (1) | 0.1553 (6) | −0.1115 (6) | 5.0 (2) |

[a] Estimated standard deviations are given in parentheses and correspond to the least significant digit(s). Positional parameters are given as fractional coordinates. $B\ (\text{Å}^2) = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$.

**Table III.** Selected Bond Distances (Å) and Angles (deg)

| | | | |
|---|---|---|---|
| | Distances | | |
| Pt–P | 2.349 (2) | C(1)–S(1) | 1.674 (6) |
| Pt–C(1) | 1.970 (6) | C(1)–S(2) | 1.651 (6) |
| Pt–S(1) | 2.337 (2) | P–C(11) | 1.835 (6) |
| Pt–S(2) | 2.383 (2) | P–C(21) | 1.892 (7) |
| | | P–C(31) | 1.875 (7) |
| | Angles | | |
| P–Pt–S(1) | 114.51 (6) | S(1)–C(1)–S(2) | 133.3 (4) |
| P–Pt–C(1) | 159.2 (2) | Pt–P–C(11) | 113.9 (2) |
| P–Pt–S(2) | 95.86 (5) | Pt–P–C(21) | 111.6 (2) |
| C(1)–Pt–S(1) | 44.7 (2) | Pt–P–C(21) | 108.9 (2) |
| C(1)–Pt–S(2)′ | 104.9 (2) | C(11)–P–C(21) | 101.5 (3) |
| Pt–C(1)–S(2) | 147.3 (4) | C(11)–P–C(31) | 108.8 (3) |
| C(1)–S(2)–Pt′ | 107.8 (2) | C(21)–P–C(31) | 112.0 (4) |

The crystal chosen for data collection was mounted on an Enraf-Nonius CAD4F diffractometer. Three standard reflections, monitored every 3.8 h during data collection, showed no decomposition had occurred. Details of the experimental conditions are summarized in Table I. Eight crystal faces were identified as the forms ⟨100⟩, ⟨010⟩, and ⟨011⟩.

A total of 3097 reflections were measured. The recorded intensities were corrected for Lorentz and polarization effects, and a standard deviation *σ*(*I*) was assigned to each intensity (*I*), by using the data reduction program of the SPD package.[11] The data were corrected for absorption by using the Gaussian method (12 × 6 × 6 grid). Transmission coefficients varied from 0.518 to 0.425 with an average correction of 0.471. Of the data collected, 2460 unique data with $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

**Structure Solution and Refinement.** The positional coordinates for the Pt atom were readily obtained from a three-dimensional Patterson synthesis. A series of difference Fourier syntheses and least-squares refinements revealed the positions of the remaining 18-nonhydrogen atoms.

The structure refinement, by full-matrix least-squares techniques on *F*, proceeded smoothly. Hydrogen atoms were included in the final cycles but not refined. Idealized positional coordinates for the H atoms were computed by assuming either sp$^2$ or sp$^3$ staggered geometries and C–H bond distances of 0.95 and 1.0 Å, respectively. The re-

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Table IV. Summary of NMR[a] and IR Spectroscopic Data

| complex | $\delta(^{31}P)^{a,b}$ | $\|^1J(^{195}Pt-^{31}P)\|$ | $\|^4J(P-Pt-C-S-^{195}Pt)\|$ | $\|^5J(^{31}P-Pt-C-S-Pt-^{31}P)\|$ | $\nu(CS_2)$, cm$^{-1}$ |
|---|---|---|---|---|---|
| $Pt_2(\mu-CS_2)_2(P(t-Bu)_2Ph)_2$[c] | 61.41 | 3227.30 | 50.5 | 51.0 | 1121 (s), 740 (m) |
| $Pt_2(\mu-CS_2)_2(P(t-Bu)_3)_2$[c,e] | 75.80 | 3141.80 | 50.1 | 51.5 | 1113 (s), 744 (m) |
| $Pd_2(\mu-CS_2)_2(P(t-Bu)_2Ph)_2$[d] | 64.51 | | | | 1150 (vs), 744 (m)<br>1110 (vs), 710 (s) |
| $Pd_2(\mu-CS_2)_2P(t-Bu_3)_2$[d] | 81.21 | | | | 1175 (s), 1150 (s)<br>1125 (vs), 715 (m) |

[a] Chemical shifts are downfield from $H_3PO_4$. [b] Spectra recorded in $CH_2Cl_2/CS_2$ with external $P(OMe)_3$ in $CO(CD_3)_2$ as reference. [c] The $^{31}P$ NMR was run on the Varian XL200 instrument at 81 MHz. [d] The $^{31}P$ NMR was run on the Bruker WP80 instrument at 32.3 MHz. [e] Prepared by the reaction of $Pt(P(t-Bu)_3)_2 + CS_2$ as in ref 4, originally formulated as $Pt_3(CS_2)_3(P(t-Bu)_3)_3$.

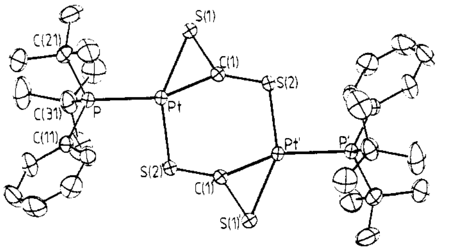

**Figure 1.** ORTEP drawing of $Pt_2(\mu-CS_2)_2(P(t-Bu)_2Ph)_2$ plotted as 50% probability thermal ellipsoids, with H atoms omitted.

finement converged at $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.0273$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0361$ (2460 unique data and 172 variables).

In the final cycle no shift exceeded 0.04 of its standard deviation. The error in an observation of unit weight is 1.15 electrons. A statistical analysis of $R_2$ over various ranges of $|F_o|$, $\lambda^{-1}$ sin $\theta$, and reflection parities showed no abnormal trends. A total difference Fourier syntheses calculated from the final structure factors contained no features of chemical significance. Final positional and $B$ thermal parameters for the non-hydrogen atoms are given in Table II. Anisotropic thermal parameters, hydrogen atom parameters, and structure amplitudes, as $10|F_o|$ and $10|F_c|$ in electrons, have been deposited as supplementary material.

## Results and Discussion

**Description of the Structure of $Pt_2(\mu-CS_2)_2(P(t-Bu)_2Ph)_2$ (2).** The crystal structure consists of discrete dimeric molecules, for the closest intermolecular distance is 2.16 Å between H12C(12) and H331C(33) in the equivalent position ($x - 1$, $y$, $z$). Selected intramolecular dimensions for the complex are presented in Table III. A perspective view of the molecule together with the atom-numbering scheme is given in Figure 1.

The complex sits on a crystallographic center of inversion. The two centrosymmetrically related $Pt(P(t-Bu)_2Ph)$ fragments are held together by two doubly bridging $CS_2$ moieties. Each $CS_2$ group is $\pi$ bonded through a C=S linkage to one metal atom and $\sigma$ bonded to the other through the exo S atom, resulting in a six-membered ring. A weighted least-squares plane calculation reveals the planarity of the $PPt(\mu-CS_2)_2PtP$ core (largest deviation 0.016 (1) Å). It was noted[3] in the report on the structure of the Ni analogue **1** that this planarity is consistent with an overall electronic delocalization and probably accounts for the general stability of the complexes.

The coordination about the Pt atom is essentially planar. The angles subtended at the Pt atom are consistent with a distorted square-planar coordination geometry.[3] The Pt–P distance, 2.349 (2) Å, is significantly longer than the value of 2.252 (1) Å found in $Pt(P(t-Bu)_2Ph)_2$;[12] however, all other dimensions associated with the phosphine ligand are normal. The Pt–P distance is comparable with that found in $Pt(\eta^2-CS_2)(PPh_3)_2$[13], 2.346 (10) Å, for the stereochemically equivalent phosphine ligand relative to the $CS_2$ ligand. The slight lengthening of the Pt–P bond is thus ascribed to the influence of the $CS_2$ ligand. A much shorter distance was found in $Pt(\pi-CS_2)(PPh_3)_2$, 2.240 (15) Å, for the phosphine in the position occupied by the S(2)′ atom in the dimer.

The Pt–C(1) and Pt–S(1) distances, 1.970 (6) and 2.337 (2) Å, respectively, are equivalent to those found in the monomer $Pt(\eta^2-CS_2)(PPh_3)_2$, 2.064 (46) and 2.328 (16) Å. The two C–S bond lengths, 1.651 (6) and 1.674 (6) Å, are not significantly different nor do they differ statistically from the values reported for the monomer $\pi$-$CS_2$ complex.[13] An S–C–S angle of 133.3 (4)° is normal.[3,13] Thus, the $\sigma$ bonding of the exo S atom and the geometric requirements of a six-membered ring have not significantly altered the geometry of the $CS_2$ ligand.

**Reaction of $M_3(CO)_3L_3$ with $CS_2$ (M = Pt, L = $P(t-Bu)_2Ph$; M = Pd, L = $P(t-Bu)_2Ph$, $P(t-Bu)_3$).** While the chemistry of mononuclear palladium(0) and platinum(0) complexes has been extensively studied,[15] very little has been reported about the reactivity of the corresponding trinuclear species. Our interest in the stability of the triangular metal framework of the complexes $M_3(CO)_3L_3$, to fragmentation in the presence of excess ligand, led us to investigate their reactions with $CS_2$. Addition of $CS_2$ to the trinuclear complexes in hexane results in rapid and quantitative conversion to the dinuclear doubly $CS_2$-bridged compounds $M_2(\mu-CS_2)_2L_2$.

Spectroscopic data for the $CS_2$ complexes are presented in Table IV. The products exhibit strong infrared absorptions in the region 1110–1175 cm$^{-1}$, which is typical of bidentate dithio ester complexes.[3,14] The Ni complex **1** has a band at 1120 cm$^{-1}$. The Pd and Pt dimers also have $CS_2$-related vibrations in the 650–750-cm$^{-1}$ region that were not observed in **1**. Previous researchers have assigned the 600–750- and 1100–1200-cm$^{-1}$ regions to the $\overline{M-C-S}$ ring and exo C=S vibrations, respectively.[16] As a general observation, complexation of the exo S atom in mononuclear $\eta^2$-$CS_2$ complexes is reflected in a slight lowering of the exo C=S frequency and a raising of the frequency assigned to the in-ring vibration.

A single P resonance is observed in the $^{31}P$ NMR spectra of the complexes. Inner and outer $^{195}Pt$ satellites, in the spectrum of complex **2**, are only consistent with a dimeric structure. The large $|^4J(^{31}P-Pt-C-S-^{195}Pt)|$ and $|^5J(^{31}P-Pt-C-SPt-^{31}P)|$ coupling constants also suggest delocalization of electron density in the $PPt(\mu-CS_2)_2PtP$ core, as noted in the structural results.

The added information available in the $^{195}Pt$ satellites of the $^{31}P$ NMR spectra allowed us to monitor changes in nuclearity during the course of the reaction of $Pt_3(CO)_3(P(t-Bu)_2Ph)_3$ with $CS_2$. As a $CH_2Cl_2/CS_2$ solution of the trimer was warmed from −50 °C, no reaction occurred until −25 °C.

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At this temperature a mononuclear complex ($\delta(^{31}P)$ 62.2 ($^1J(^{31}P-^{195}Pt)$ = 2600 Hz)) begins to appear. When the temperature is increased to −10 °C, a second species forms that is dinuclear with two equivalent phosphine environments ($\delta(^{31}P)$ 60.9 ($^1J(^{31}P-^{195}Pt)$ = 2630 Hz, $|J(^{31}P-Pt\cdots{}^{195}Pt)|$ = 17 Hz, $|J(^{31}P-Pt\cdots{}^{31}P)|$ = 15 Hz). The product **2** forms at 0 °C. We have no other information about the nature of the two intermediates but are confident that the reaction proceeds via a mononuclear pathway. The reaction of $Pt_3(CO)_3(P(t\text{-}Bu)_3)_3$ with $CS_2$ is very much slower than the aforementioned examples and appears to produce a mixture of products. We are currently examining this reaction to try to elucidate the nature of the intermediates.

The reaction of $Pt(P(t\text{-}Bu)_3)_2$ with $CS_2$ has recently been reported.[4] Single crystals could not be obtained, and thus the complex formed was postulated as $Pt_3(CS_2)_3(P(t\text{-}Bu)_3)_3$ on the basis of analytical, IR, and molecular weight data. We prepared this complex and report the $^{31}P$ NMR data in Table IV. The $^{195}Pt$ satellite pattern unequivocally demonstrates that the complex is dimeric and, on the basis the similarity with **2**, is in fact $Pt_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_3)_2$. $Pt(P(t\text{-}Bu_2)Ph)_2$ reacts with $CS_2$ to produce **2**. We have also found that bis(phosphine)palladium(0) complexes react with $CS_2$ to produce either mononuclear $Pd(\eta^2\text{-}CS_2)L_2$ or dinuclear $Pd_2(\mu\text{-}CS_2)_2L_2$ complexes (L = a phosphine ligand) depending upon the nature of the phosphine ligand.[17]

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**Registry No.** **2**, 91686-59-8; $Pt_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_3)_2$, 91686-60-1; $Pd_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_2Ph)_2$, 91686-61-2; $Pd_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_3)_2$, 91686-62-3; $Pt_3(CO)_3(P(t\text{-}Bu)_2Ph)_3$, 62931-81-1; $Pt_3(CO)_3(P(t\text{-}Bu)_3)_3$, 79138-89-9; $Pd_3(CO)_3(P(t\text{-}Bu)_2Ph)_3$, 62931-80-0; $Pd_3(CO)_3(P(t\text{-}Bu)_3)_3$, 62931-79-7; $Pt(P(t\text{-}Bu)_3)_2$, 60648-70-6; $Pt(P(t\text{-}Bu)_2Ph)_2$, 59765-06-9; $CS_2$, 75-15-0.

**Supplementary Material Available:** Listings of weighted least-squares plane data for $PPt(CS_2)_2PtP$ core, hydrogen atom parameters, anisotropic thermal parameters, and structure amplitudes as $10|F_o|$ vs. $10|F_c|$ (16 pages). Ordering information is given on any current masthead page.

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Contribution from Rocketdyne, A Division of
Rockwell International, Canoga Park, California 91304

# Synthesis and Characterization of Bis[difluorooxychlorine(V)] Hexafluoronickelate(IV), $(ClF_2O)_2NiF_6$

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It is well-known that $ClF_3O$ can form with strong Lewis acids, such as $BiF_5$, $SbF_5$, $AsF_5$, $PF_5$, $TaF_5$, $NbF_5$, $VF_5$, $PtF_5$, $UF_5$, $SiF_4$, $BF_3$, HF, and $MoF_4O$, adducts containing the $ClF_2O^+$ cation.[1-6] All these adducts have been prepared by the direct combination of $ClF_3O$ with the corresponding Lewis acids. The purpose of this study was to examine whether $ClF_2O^+$-containing salts derived from unstable Lewis acids, such as $NiF_4$, can be prepared by the indirect metathetical methods developed for $NF_4^+$ salt chemistry.[7]

## Experimental Section

**Materials and Apparatus.** Literature methods were used for the syntheses of $Cs_2NiF_6$[7] and $ClF_2OSbF_6$[4] and the drying of the HF solvent.[8] Volatile materials were manipulated in a well-passivated (with $ClF_3$) stainless-steel Teflon FEP vacuum system.[9] Solids were handled in the dry-$N_2$ atmosphere of a glovebox.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points.[10,11] Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and a Spex Model 1403 spectrophotometer using the 6471-Å exciting line of a Kr ion laser and premonochromators for the elimination of plasma lines. Sealed quartz tubes were used as sample containers. The low-temperature spectra were recorded by using a previously described device.[12]

**Synthesis of $(ClF_2O)_2NiF_6$.** A mixture of $ClF_2OSbF_6$ (7.008 mmol) and $Cs_2NiF_6$ (3.505 mmol) was loaded in the drybox into a previously described[10] double-U-tube filter apparatus. Dry HF (185 mmol) was condensed at −196 °C into the apparatus on the vacuum line, and the mixture was warmed for 30 min to 25 °C with agitation. The apparatus was cooled to −78 °C and inverted, and the solid and liquid phases were separated by filtration assisted by 2 atm of dry $N_2$ gas. The material volatile at 25 °C was pumped off for 12 h and consisted mainly of HF. The filter cake (2.768 g; weight calculated for 7.01 mmol of $CsSbF_6$, 2.584 g) was shown by vibrational spectroscopy to consist of mainly $CsSbF_6$ containing small amounts of $ClF_2O^+$[11] and $NiF_6^{2-}$.[7] The filtrate residue (965 mg; weight calculated for 3.505 mmol of $(ClF_2O)_2NiF_6$, 1.232g, corresponding to a 78% yield) was shown by elemental analysis and vibrational spectroscopy to have the following composition (wt %): $(ClF_2O)_2NiF_6$, 93.04; $ClF_2OSbF_6$, 1.49; $CsSbF_6$, 5.47. Anal. Calcd: Ni, 15.54; Cl, 18.93; Cs, 1.97; Sb, 2.36. Found: Ni, 15.6; Cl, 18.7; Cs, 2.07; Sb, 2.48. The losses of $(ClF_2O)_2NiF_6$ can be attributed mainly to hang-up of some $(ClF_2O)_2NiF_6$ on the filter cake.

## Results and Discussion

**Synthesis and Properties of $(ClF_2O)_2NiF_6$.** The metathetical process previously developed for $(NF_4)_2NiF_6$[7] has successfully been transferred to the synthesis of $(ClF_2O)_2NiF_6$ according to

$$2ClF_2OSbF_6 + Cs_2NiF_6 \xrightarrow[-78\ °C]{\text{HF solution}} 2CsSbF_6\downarrow + (ClF_2O)_2NiF_6$$

The new compound $(ClF_2O)_2NiF_6$ is a deep purple crystalline solid that is stable at 60 °C under a dynamic vacuum. At 110 °C the observed decomposition rate was about 25%/h. The main decomposition products, volatile at ambient temperature but condensible at −196 °C, were $ClF_3O$ and a small amount of $FClO_2$ (arising from handling of the $ClF_3O$) as shown by their $^{19}F$ NMR and infrared spectra.[11] An exhaustive pyrolysis of a sample in a sapphire reactor at 110 °C under a dynamic vacuum resulted in quantitative $ClF_3O$ evolution and the

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