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Reactivity of 16- and 18-Electron Mixed Platinum-Gold Clusters with Halides. Crystal and Molecular Structures of $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]\cdot 2C_4H_{10}O$

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In the reaction of the 16-electron cluster $[Pt(AuPPh_3)_8](NO_3)_2$ with X^- (X = I, SCN, Cl) $[Pt(PPh_3)(AuPPh_3)_6(AuX)_3]$ is formed in about 40% yield. The crystal and molecular structures of $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]\cdot 2C_4H_{10}O$ have been investigated by X-ray analysis (monoclinic, space group $P2_1/n$, a = 15.938 (4) Å, b = 52.764 (14) Å, c = 16.747 (4) Å, β = 105.06 (3)°, V = 13 600 Å^3, Z = 4, Cu Kα radiation). The residuals are R = 0.060 and R_w = 0.068 for 8243 observed reflections and 466 variables. The symmetry of the metal cluster is C_{3v}. In the metal cluster the central Pt atom is surrounded by six $AuPPh_3$ groups, three AuCl groups, and one phosphine. The reaction of the 18-electron systems $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ and $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ with NBu_4^+ halides leads to the substitution of one Au-bonded PPh_3 and the formation of respectively $[Pt(CO)(AuPPh_3)_7(AuX)]^+$ and $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$ (X = Cl, Br, I). The products are characterized by elemental analysis and ^{31}P, ^{195}Pt, and ^{13}C NMR spectroscopy and are discussed in terms of the electronegativity of the ligand X. The reactions of $[Pt(H)(AuPPh_3)_8]^+$ and $[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$ with Cl^-, Br^-, or I^- lead to a decomposition of the clusters.

Introduction

In platinum-gold clusters the number of cluster valence electrons is a major factor in determining structure and reactivity. For the peripheral groups only the inpointing σ orbitals are involved. $AuPPh_3$, H, halides, and CN donate 1 electron; CO and PPh_3, 2; AuX, 0; and the central Pt atom contributes 10 to the electron count. This electron count determines structure and reactivity[1-6] of the compounds. Clusters with 16 valence electrons have a toroidal geometry and undergo nucleophilic as well as electrophilic additions. Clusters with 18 electrons have a spheroidal geometry and only undergo electrophilic additions. The reaction of the 16-electron cluster $[Pt(AuPPh_3)_8]^{2+}$ with 2 equiv of CN^- ligands leads via fragmentation and growth to $[Pt(CN)(AuPPh_3)_8(AuCN)]^+$.[1] We think that there is a nucleophilic attack of CN^- on the central Pt atom, followed by a fragmentation of the cluster and the formation of $Au(CN)_2^-$. The oxidative addition of $Au(CN)_2^-$ to $[Pt(AuPPh_3)_8]^{2+}$ yielding $[Pt(CN)(AuPPh_3)_8(AuCN)]^+$ has been reported before.[1]

The reactivity of 18-electron clusters toward CN^- looks less complicated. A nucleophilic addition to the central Pt seems not to be possible, and only substitution of one or two of the Au-bonded phosphines is found to occur. The reaction of 2 equiv of CN^- with $[Pt(CO)(AuPPh_3)_8]^{2+}$ leads to formation of $Pt(CO)(AuPPh_3)_6(AuCN)_2$. With more CN^- the clusters are decomposed. Kanters[2] investigated the reaction of platinum-gold clusters with CNR (R = *i*-Pr, *t*-Bu). In the reaction of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with CNR $[Pt(CO)(AuPPh_3)_7(AuCNR)]^{2+}$ is formed. In order to know more about the reactivity toward halides and pseudohalides, it is of interest to investigate the reactions of 16- and 18-electron systems with halides and to compare them with the CN^- and the CNR reactions.

Experimental Section

General Procedures. Analyses were carried out at the analytical laboratory of this university and at the Analytical Laboratory, Engelskirchen, FRG. ICP measurements in DMSO solutions were done on a Plasma 200 ICP-AE apparatus to give Pt:Au:P ratios. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker CPX-300 NMR spectrometer at 121.44 MHz and on a Bruker WM-200 spectrometer at 81.02 MHz in CH_2Cl_2 solutions and with TMP/CD_2Cl_2 as an external reference. $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker WM-200 NMR spectrometer at 43.02 MHz in CD_2Cl_2 solutions with K_2PtCl_6 in D_2O as an external reference. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker WM-200 NMR spectrometer at 50.32 MHz in CD_2Cl_2 versus TMS as external reference. The IR spectra of CsI pellets were recorded on a Perkin-Elmer 1720-X infrared Fourier transform spectrometer. Fast atom bombardment mass spectroscopy (FAB-MS) measurements were carried out at the Mass Spectrometry Service Laboratory in the University of Minnesota, using a V.G. Analytical Ltd 7070 E-HF high-resolution double-focusing mass spectrometer. A *m*-nitrobenzyl matrix was used, and mass calibrations were achieved with reference spectra of CsI clusters.[7]

Preparations. $[Pt(AuPPh_3)_8](NO_3)_2$, $[Pt(CO)(AuPPh_3)_8](NO_3)_2$, $[Pt(CO)(Ag)(AuPPh_3)_8](NO_3)_3$, $[Pt(H)(AuPPh_3)_8](NO_3)$, and $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ were prepared according to the literature.[3,4,8,9] All solvents were of reagent grade and were used without further purification.

$[Pt(PPh_3)(AuPPh_3)_6(AuI)_3]$. To a solution of 100 mg (2.5 × 10^{-2} mmol) of $[Pt(AuPPh_3)_8](NO_3)_2$ in acetone at 50 °C is added 18.5 mg (5.0 × 10^{-2} mmol) of Bu_4NI with stirring. Within a few minutes a brown precipitate is formed. After 2 h the mixture is cooled to room temperature and the brown solid is filtered off. The solid is extracted with CH_2Cl_2 to get a red solution. The red solution is filtered. Red crystals are formed by adding diethyl ether to the CH_2Cl_2 solution until the solution became cloudy, after which it was allowed to stand overnight. The red crystals are filtered off, washed with diethyl ether, and dried in vacuo. Yield: 46 mg (0.011 mmol). Anal. Calcd for $Au_9C_{126}H_{105}I_3P_7Pt$ (M_r 4184.6): C, 35.73; H, 2.55; Pt, 4.66; Au, 42.36; P, 5.18; I, 9.10. Found: C, 36.17; H, 2.53; Pt, 4.73; Au, 42.30; P, 4.95; I, 9.28. $^{31}P\{^1H\}$ NMR: δ near 37.6 ppm (multiplet), $^1J(^{195}Pt-^{31}P)$ = 2700 Hz, δ near 43 ppm, $^2J(^{195}Pt-^{31}P) \approx$ 290 Hz, and a more complicated pattern near 43 ppm.

$[Pt(PPh_3)(AuPPh_3)_6(AuSCN)_3]$. The same procedure as for $[Pt(PPh_3)(AuPPh_3)_6(AuI)_3]$ is followed but with Bu_4NSCN instead of Bu_4NI. Yield: 18.2 mg (0.0046 mmol). Anal. Calcd for $Au_9C_{129}H_{105}N_3P_7PtS_3$ (M_r 3978.1): C, 38.70; H, 2.81; N, 1.07. Found: C, 38.90; H, 2.66; N, 1.06. ICP: Pt:Au:P = 1.0:9.1:7.0. IR: 2103 cm^{-1}, ν_{CN}. $^{31}P\{^1H\}$ NMR: δ 47.9 ppm, $^1J(^{195}Pt-^{31}P)$ = 2570 Hz, δ = 42.3 ppm, $^2J(^{195}Pt-^{31}P)$ = 286 Hz, and a more complicated pattern near 43 ppm. FABMS (*m*-nitrobenzyl alcohol matrix): m/z 3978 ($[Pt(PPh_3)(AuPPh_3)_6(AuI)_3]^+ = M^+$), 3920 ($(M - SCN)^+$), 3658 ($(M - SCN - PPh_3)^+$), 3461 ($(M - SCN - PPh_3 - Au)^+$), 3403 ($(M - 2SCN - PPh_3 - Au)^+$).

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$[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]$. The same procedure as for $[Pt(PPh_3)(AuPPh_3)_6(AuI)_3]$ is followed but now with Et_4NCl instead of Bu_4NI. Yield: 63 mg (0.016 mmol). Anal. Calcd for $Au_9C_{126}Cl_3H_{105}P_7Pt$ (M_r 3910.2): C, 38.76; H, 2.88. Found: C, 38.70; H, 2.71. ICP: Pt:Au:P = 1.0:9.1:7.3. IR: 260 cm^{-1}, AuCl stretch absorption band. $^{31}P\{^1H\}$ NMR: strong resonance at 41.2 ppm with Pt satellites at 289 Hz, two other resonances at 42.7 and 43.5 ppm with coupling constants of about 290 Hz, and an even multiplet at 39 ppm with $^1J(Pt–P)$ coupling constant of 2614 Hz.

$[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]\cdot 2C_4H_{10}O$. X-ray-quality crystals could be obtained from a mixture of dichloromethane and diethyl ether containing $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]$. In the reaction of $[Pt(AuPPh_3)_8]^{2+}$ with X^-, $[Pt(PPh_3)(AuPPh_3)_7]^+$ and $PPh_3Au(NO_3)$ are formed as byproducts.

$[Pt(CO)(AuPPh_3)_7(AuI)](NO_3)$. To a solution of 50 mg (1.25×10^{-2} mmol) of $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ in 7 mL of acetone is added 1.1 equiv (5.1 mg, 1.38×10^{-2} mmol) of Bu_4NI. The mixture is stirred for 6 h at room temperature. The solution is evaporated to dryness. The red-yellow solid is dissolved in CH_2Cl_2 and crystallized by adding diethyl ether. Yield: 45 mg (1.2×10^{-2} mmol). Anal. Calcd for $Au_8C_{127}H_{105}INO_4P_8Pt$ (M_r 3823.8): C, 39.89; H, 2.77; N, 0.36. Found: C, 39.48; H, 2.83; N, 0.35. ICP: Pt:Au:P = 1.0:8.0:7.0. IR: CO vibration at 1948 cm^{-1} and NO_3^- vibrations at 1360 cm^{-1} (free NO_3^-). $^{31}P\{^1H\}$ NMR: $\delta = 51.6$ ppm, $^2J(^{195}Pt–^{31}P) = 384.1$ Hz. $^{195}Pt\{^1H\}$ NMR: $\delta = -5535$ ppm (octet), $^2J(^{195}Pt–^{31}P) = 384.1$ Hz. With a 10-fold excess of I^- no other products are found.

$[Pt(CO)(AuPPh_3)_7(AuI)](PF_6)$. To a solution of 50 mg (1.3×10^{-2} mmol) of $[Pt(CO)(AuPPh_3)_7(AuI)](NO_3)$ in 10 mL of methanol is added 20 mg (3×10^{-2} mmol) of Bu_4NPF_6. A yellow precipitate is formed. The precipitate is filtered off and dissolved in CH_2Cl_2. After addition of diethyl ether, red crystals are formed. Yield: 35 mg (0.75×10^{-2} mmol). Anal. Calcd for $Au_8F_6C_{127}H_{105}IOP_8Pt$ (M_r 3906.8): C, 39.04; H, 2.71; I, 3.25. Found: C, 38.99; H, 2.73; I, 3.19. ICP: Pt:Au:P = 1.0:8.0:7.9. IR: PF_6 frequency at 840 cm^{-1} and CO vibration at 1948 cm^{-1}.

$[Pt(^{13}CO)(AuPPh_3)_7(AuI)](NO_3)$. The same procedure as for $[Pt(CO)(AuPPh_3)_7(AuI)]NO_3$ is used, but as starting material, $[Pt(^{13}CO)(AuPPh_3)_8](NO_3)_2$ is used. IR: ^{13}CO vibration at 1902 cm^{-1} and free NO_3^- at 1360 cm^{-1}. $^{31}P\{^1H\}$ NMR: $\delta = 51.6$ ppm (doublet), $^3J(^{31}P–^{13}C) = 10.5$ Hz, $^2J(^{195}Pt–^{31}P) = 384.1$ Hz. $^{13}C\{^1H\}$ NMR: $\delta = 208$ ppm (octet), $^3J(^{31}P–^{13}C) = 10.5$ Hz, $^1J(^{195}Pt–^{13}C) = 1025$ Hz.

$[Pt(CO)(AuPPh_3)_7(AuBr)](NO_3)$. The same procedure as for $[Pt(CO)(AuPPh_3)_7(AuI)]NO_3$ is used but with Bu_4NBr (4.9 mg) instead of Bu_4NI. $^{31}P\{^1H\}$ NMR: $\delta = 51.7$ ppm, $^2J(^{195}Pt–^{31}P) = 383.9$ Hz. IR: NO_3^- vibration at 1360 cm^{-1} and CO at 1949 cm^{-1}.

$[Pt(CO)(AuPPh_3)_7(AuCl)](NO_3)$. The same procedure as for $[Pt(CO)(AuPPh_3)_7(AuI)]NO_3$ is used but now with Bu_4NCl (2.3 mg). $^{31}P\{^1H\}$ NMR: $\delta = 52.4$ ppm, $^2J(^{195}Pt–^{31}P) = 379.1$ Hz. IR: NO_3^- vibration at 1360 cm^{-1} and CO at 1949 cm^{-1}.

$[Pt(CO)(AuPPh_3)_7(AuOR)](OR)$ ($R = CH_3$, H). To a solution of 50 mg of $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ (1.25×10^{-2} mmol) in 20 mL of methanol is added 500 mg (8 mmol) of KOH. After 15 min the solution is evaporated to dryness. The red solid is dissolved in CH_2Cl_2, the solution is filtered, and the CH_2Cl_2 is evaporated. IR: $\nu(CO)$ at 1966 cm^{-1} and no CH_3 and OH^- vibrations found. $^{31}P\{^1H\}$ NMR: $\delta = 52.3$ ppm, $^2J(^{195}Pt–^{31}P) = 379.2$ Hz. ^{195}Pt NMR: $\delta = -5678$ ppm (octet), $^2J(^{195}Pt–^{31}P) = 379.2$ Hz, no Pt–H coupling detectable. In the NMR spectra always some $Pt(CO)(AuPPh_3)_8(NO_3)_2$ was found to be present; purification was not successful. ^1H NMR spectra in the region of OH or CH_3 were not decisive.

$[Pt(H)(PPh_3)(AuPPh_3)_6(AuI)]NO_3$. To a solution of 50 mg (1.32×10^{-2} mmol) of $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ in 7 mL of acetone is added 5.4 mg (1.45×10^{-2} mmol) of Bu_4NI. After being stirred for 6 h, the mixture is evaporated to dryness. NMR spectra show that from recrystallization of methanol/ether, dichloromethane/ether, or acetone/ether solutions only impure products could be obtained. ICP: Pt:Au:P = 1.0:7.0:7.1. IR: NO_3^- frequency at 1360 cm^{-1}. $^{31}P\{^1H\}$ NMR: $\delta = 46.7$ ppm (doublet), $^3J(^{31}P–^{31}P) = 27.6$ Hz, $^2J(^{195}Pt–^{31}P) = 379$ Hz, $\delta = 55.2$ ppm (septet), $^3J(^{31}P–^{31}P) = 27.6$ Hz, $^1J(^{195}Pt–^{31}P) = 2735$ Hz. ^{195}Pt NMR: $\delta = -5541$ ppm, $^1J(^{195}Pt–^1H) = 606$ Hz, $^1J(^{195}Pt–^{31}P) = 2735$ Hz, $^2J(^{195}Pt–^{31}P) = 379$ Hz. ^1H NMR: $\delta = 1.3$ ppm, $^1J(^{195}Pt–^1H) = 606$ Hz, $^2J(^{31}P–^1H) = 7$ Hz.

$[Pt(H)(PPh_3)(AuPPh_3)_6(AuI)](PF_6)$. To a solution of 50 mg (1.6×10^{-2} mmol) of $[Pt(H)(PPh_3)(AuPPh_3)_6(AuI)](NO_3)$ dissolved in 3 mL of methanol is added 7 mg (1.8×10^{-2} mmol) of Bu_4NPF_6. The red precipitate formed is filtered off and washed with methanol. Yield: 29 mg (0.9×10^{-2} mmol). IR: free PF_6^- absorption at 840 cm^{-1}. NMR: the same as for $[Pt(H)(PPh_3)(AuPPh_3)_6(AuI)](NO_3)$.

Table I. Crystal Data for $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]\cdot 2C_4H_{10}O$

chem formula	$C_{134}H_{105}O_2P_7Au_9PtCl_3$	space group	$P2_1/n$ (No. 14)
fw	4058.4	T	20 °C
a	15.938 (4) Å	λ	1.541 838 Å
b	52.764 (14) Å	ρ_{calc}	1.778 g/cm^3
c	16.747 (4) Å	μ(Cu Kα)	182.48 cm^{-1}
β	105.06 (3)°	$R(F_o)^a$	0.060
V	13600 Å^3	$R_w(F_o)^b$	0.068
Z	4		

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$.

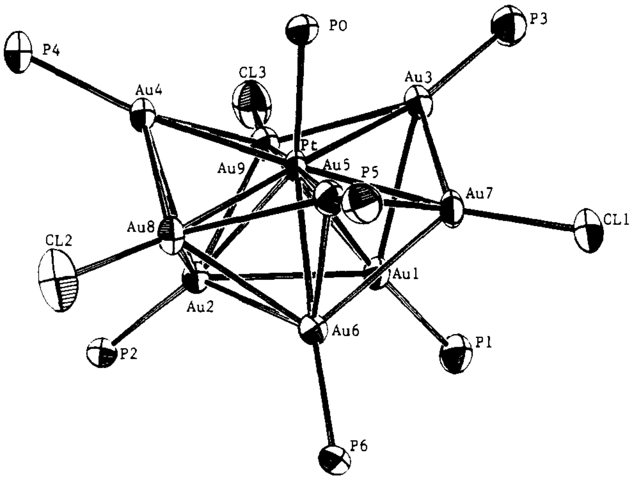

Figure 1. ORTEP[12] plot of $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]\cdot 2C_4H_{10}O$ with use of 50% probability ellipsoids. Phenyl groups are omitted for the sake of clarity.

$[Pt(H)(PPh_3)(AuPPh_3)_6(AuBr)](NO_3)$ and $[Pt(H)(PPh_3)(AuPPh_3)_6(AuCl)](NO_3)$. The same synthesis as for $[Pt(H)(PPh_3)(AuPPh_3)_6(AuI)](NO_3)$ is followed but now with Bu_4NBr and Bu_4NCl, respectively. Complete purification of the products could not be achieved. In the ^{31}P NMR spectra the presence of some $AuPPh_3X$ (X = Cl, Br) and unknown products with $\delta = 50.2$ and 52.2 ppm was detected.

$[Pt(H)(PPh_3)(AuPPh_3)_6(AuBr)](NO_3)$. IR: 1360 cm^{-1}, free NO_3^-. $^{31}P\{^1H\}$ NMR: $\delta = 46.6$ ppm (doublet), $^3J(^{31}P–^{31}P) = 29.1$ Hz, $^2J(^{195}Pt–^{31}P) = 378$ Hz, $\delta = 54.2$ ppm (septet), $^3J(^{31}P–^{31}P) = 29.1$ Hz. $^1J(^{195}Pt–^{31}P)$ Pt satellites could not be assigned with certainty.

$[Pt(H)(PPh_3)(AuPPh_3)_6(AuCl)](NO_3)$. IR: 1360 cm^{-1}, free NO_3. $^{31}P\{^1H\}$ NMR: $\delta = 46.6$ ppm (doublet), $^3J(^{31}P–^{31}P) = 30.3$ Hz, $^2J(^{195}Pt–^{31}P) = 374$ Hz, $\delta = 50.0$ ppm (septet), $^3J(^{31}P–^{31}P) = 30.3$ Hz.

The reaction of $[Pt(H)(AuPPh_3)_8]^+$ with halides was investigated with the same procedure as described above. Several products were found to be present. In the ^{31}P NMR spectra $[Au(PPh_3)_2]NO_3$, PPh_3, $[Pt(PPh_3)(AuPPh_3)_6]^{2+}$, and $[Pt(AuPPh_3)_8]^{2+}$ could be identified but also unknown products with chemical shifts in CH_2Cl_2 solutions of 51.4 and 52.5 ppm. Attempts of further purification were unsuccessful.

In the reaction of $[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$ with 1 equiv of iodide, $[Pt(CO)(AuPPh_3)_8]^{2+}$, $[Pt(CO)(AuPPh_3)_7(AuI)]^+$, and unknown products with chemical shifts in CH_2Cl_2 solutions of 54.7 and 56.8 ppm were detected in the ^{31}P NMR spectra.

The reaction of $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ with excess OH^- in methanol leads to a breakdown of the cluster with the formation of $[Au(PPh_3)_2]^+$ and $[Pt(PPh_3)(AuPPh_3)_6]^{2+}$ (detected by ^{31}P NMR spectroscopy).

Structure Determination of $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]\cdot 2C_4H_{10}O$. Collection and Reduction of Crystallographic Data. Since single crystals decomposed very quickly upon removal from the solvent mixture, a crystal of $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]\cdot 2C_4H_{10}O$ was mounted in a capillary together with a mixture of dichloromethane and diethyl ether. X-ray data were measured on a Nonius CAD4 diffractometer. Standard experimental and computational details are given elsewhere.[10] The crystal data are listed in Table I. No extinction correction was performed.

Solution and Refinement of the Structure. The positions of the metal atoms were found by SHELXS.[11] The remaining non-hydrogen atoms were positioned from successive difference Fourier maps. The structure

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(11) Computer program references for SHELXS (Sheldrick), DIRDIF (Beurskens et al.), SHELX (Sheldrick), and DIFABS (Walker and Stuart) are given in ref 10.

Table II. Selected Fractional Positional and Thermal Parameters for $Pt(P(C_6H_5)_3)(AuP(C_6H_5)_3)_6(AuCl)_3{\cdot}2C_4H_{10}O$

atom	*x*	*y*	*z*	$100U_{eq}$,[a] Å^2
Pt	0.32766 (7)	0.11871 (3)	−0.03079 (8)	2.36 (5)
Au(1)	0.40120 (8)	0.15205 (3)	0.09625 (8)	2.78 (5)
Au(2)	0.21371 (7)	0.15308 (3)	0.01206 (8)	2.84 (5)
Au(3)	0.44852 (8)	0.09943 (3)	0.10198 (8)	3.03 (5)
Au(4)	0.16374 (8)	0.10289 (3)	−0.04965 (8)	3.18 (5)
Au(5)	0.37664 (8)	0.12872 (3)	−0.17250 (8)	3.17 (5)
Au(6)	0.34806 (8)	0.16911 (3)	−0.07091 (8)	2.88 (5)
Au(7)	0.49495 (8)	0.13228 (3)	−0.01459 (8)	3.09 (5)
Au(8)	0.20436 (8)	0.13998 (3)	−0.15784 (8)	3.21 (5)
Au(9)	0.28062 (8)	0.11192 (3)	0.11456 (8)	2.96 (5)
P(0)	0.3401 (5)	0.0768 (2)	−0.0775 (5)	3.3 (3)
P(1)	0.4765 (5)	0.1769 (2)	0.2032 (5)	3.9 (3)
P(2)	0.1075 (5)	0.1759 (2)	0.0507 (5)	3.4 (3)
P(3)	0.5370 (5)	0.0761 (2)	0.2053 (5)	4.1 (4)
P(4)	0.0315 (5)	0.0833 (2)	−0.0747 (6)	4.1 (3)
P(5)	0.4236 (6)	0.1305 (2)	−0.2902 (5)	4.1 (4)
P(6)	0.3730 (5)	0.2095 (2)	−0.1135 (5)	3.1 (3)
Cl(1)	0.6413 (5)	0.1394 (2)	−0.0096 (6)	5.1 (4)
Cl(2)	0.0914 (6)	0.1535 (2)	−0.2723 (5)	6.9 (4)
Cl(3)	0.2539 (5)	0.0997 (2)	0.2431 (5)	4.8 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$.

was refined by full-matrix least-squares with SHELX.[11] All phenyl H atoms were introduced at expected positions and refined in a riding mode (C–H = 1.00 Å). At this stage a difference Fourier map showed two independent diethyl ether molecules. One overall isotropic temperature factor (U = 0.21 (2) Å^2) was used for all phenyl H atoms. During the final stage of the refinement, the anisotropic parameters of the gold, platinum, phosphorus, and chlorine atoms were refined. Final convergence was reached at R = 0.060. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 0.6794/[\sigma^2(F_o) + 0.0005F_o^2]$. Maximum residual density was 2.2 e/Å^3 near the Pt and Au atoms. Further residual density was below 0.9 e/Å^3. Positional and thermal parameters of selected atoms are given in Table II, and selected bond distances and angles are in Table III. The molecular structure is given in Figure 1.[12]

Results

Reaction of 16-Electron Clusters with X^- (X = I, SCN, Cl). From the reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with I^- in acetone and dichloromethane $[Pt(PPh_3)(AuPPh_3)_6(AuI)_3]$ could be isolated in 40% yield. Elemental analysis reveals a composition of $PtAu_9(PPh_3)_7I_3$. The low solubility and the lack of NO_3^- absorptions in the IR spectrum indicate that the cluster is a neutral molecule. The ^{31}P NMR spectrum is rather complex. It shows a multiplet near 37.6 ppm and a coupling of 2700 Hz, indicating a platinum–phosphorus bond. Strong resonances are found near 43 ppm, due to different $AuPPh_3$ sites, with Pt satellites and a $^2J(^{195}Pt–^{31}P)$ of 290 Hz, which is near the low limit of what is normally found (300–500 Hz). This indicates that the $Au–PPh_3$ groups are bonded to platinum, like in the parent compound.

All data indicate the cluster to have Pt in the center bonded to one PPh_3 group, six $AuPPh_3$ groups, and three AuI groups, $[Pt(PPh_3)(AuPPh_3)_6(AuI)_3]$. When the reaction was carried out with SCN^-, a product could be isolated, from which elemental analysis revealed a composition of $PtAu_9(PPh_3)_7(SCN)_3$. In the IR spectrum ν_{CN} was found at 2103 cm^{-1}, which can be correlated with the ν_{CN} = 2102 cm^{-1} of $[Au(AuPPh_3)_7(AuSCN)_3]$ in which SCN is S-coordinated to gold.[13] NMR data show a platinum–phosphine site at 47.9 ppm with $^1J(^{195}Pt–^{31}P)$ = 2570 Hz and a gold–phosphine site near 42.3 ppm ($^2J(^{195}Pt–^{31}P)$ = 286 Hz). The molecular composition was also confirmed by fast atom bombardment mass spectrometry (FAB-MS). The positive ion FAB-MS spectrum of $[Pt(PPh_3)(AuPPh_3)_6(AuSCN)_3]$ shows many peaks in the mass range of m/e 1000–4000. In the Experimental Section the highest mass peaks are given. The experimental data fit very well for the assumed composition. All data are in accord with the assumption that the cluster has Pt in the center bonded to one PPh_3 group, six $AuPPh_3$ groups, and three AuSCN groups, $[Pt(PPh_3)(AuPPh_3)_6(AuSCN)_3]$.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) of $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]$[a]

	range	mean values (sd's[b])
Pt–Au(i)	2.775–2.789	2.782 (±0.004)
Pt–Au(j)	2.682–2.736	2.727 (±0.02)
Pt–Au(k)	2.705–2.750	2.730 (±0.013)
Pt–P(0)		2.373 (9)
Au(i)–Au(i)	2.852–2.963	2.92 (±0.04)
Au(i)–Au(j)	2.837–2.879	2.863 (±0.013)
Au(i)–Au(k)	2.802–3.000	2.89 (±0.03)
Au(j)–Au(k)	2.816–2.932	2.86 (±0.02)
Au(k)–Cl	2.342–2.388	2.368 (±0.014)
Au(i)–P	2.292–2.312	2.302 (±0.006)
Au(j)–P	2.287–2.291	2.288 (±0.001)[c]
Au(i)–Pt–Au(i)	61.75–64.24	63.4 (±0.8)
Au(i)–Pt–Au(j)	61.86–63.46	62.7 (±0.5)
	112.57–119.48	115.9 (±1.0)
Au(i)–Pt–Au(k)	60.76–66.26	63.2 (±0.8)
	114.30–119.52	116.1 (±1.7)
Au(j)–Pt–Au(j)	116.06–118.60	117.1 (±0.8)
Au(j)–Pt–Au(k)	61.83–65.32	63.4 (±0.5)
	176.24–177.00	176.7 (±0.2)
Au(k)–Pt–Au(k)	115.90–117.37	116.3 (±0.5)
Au(i)–Pt–P(0)	141.9–143.8	142.6 (±0.6)
Au(j)–Pt–P(0)	79.6–80.4	80.0 (±0.2)
Au(k)–Pt–P(0)	96.6–103.6	101 (±2)
Pt–Au(k)–Cl	170.4–173.2	172.1 (±0.9)
Pt–Au–P	169.1–174.1	171.5 (±0.8)

[a] Because of local C_{3v} symmetry, the following atoms are symmetry related: Au(1) = Au(2) = Au(6) = Au(i); Au(3) = Au(4) = Au(5) = Au(j); Au(7) = Au(8) = Au(9) = Au(k). See Figure 1. [b] $sd = [\{\sum(x - x_i)^2/n(n-1)\}]^{1/2}$; $x = (\sum x_i)/n$. [c] Note that the esd from the structure refinement is much larger, i.e. 0.005; esd = $\{\sum\sigma_i^2/n^2\}$.

For the chloro compound the composition was established by elemental analysis as $PtAu_9(PPh_3)_7Cl_3$. In the IR spectrum a metal–chloride frequency was found at 260 cm^{-1}. The ^{31}P NMR spectrum is more complicated, apparently because the platinum–phosphine site and the gold–phosphine sites have nearly the same chemical shifts (near 43 ppm). The molecular structure, as determined by X-ray analysis, showed a metal in the center, surrounded by one PPh_3 group, six peripheral metal–PPh_3 groups, and three metal–chloride groups. By comparison of these data with those of $[Pt(PPh_3)(AuPPh_3)_6(AuI)_3]$ and $[Pt(PPh_3)(AuPPh_3)_6(AuSCN)_3]$, the chloro compound is described as having Pt in the center of the cluster bonded to one PPh_3 group, six $AuPPh_3$ groups, and three Au–Cl groups, $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]$.

The skeletal geometry appears to be similar to those of $[Au(AuPPh_3)_7(AuI)_3]$[14] and $[Pt(CN)((AuCN)(AuPPh_3)_8]^+$.[1] It is based on a centered icosahedron. Around the platinum center, two different $AuPPh_3$ sites and one AuCl site are present, taking up 9 of the 12 vertices. Finally, one PPh_3, directly attached to the central atom, substitutes a triangular face of the icosahedron. There is a local C_{3v} symmetry, of which the C_3 axis goes through the platinum center and through P(0). The symmetry planes σ_1, σ_2, and σ_3 are defined by the atoms P(0) and Pt and Au(1), Au(2), and Au(6), respectively. The Pt–AuCl distances (2.705–2.750 Å) are just in between the two groups of Pt–$AuPPh_3$ distances (Pt–Au(1,2,6) = 2.775–2.789 Å and Pt–Au(3,4,5) = 2.682–2.736 Å). The importance of the radial bonding is demonstrated by the short radial Au–Au distances (2.68–2.79 Å). Radial as well as tangential distances are about the same as those of the $[Pt(CN)(AuCN)(AuPPh_3)_8]^+$ cluster (Pt–Au = 2.690–2.734 Å) and (Au–Au = 2.860–3.041 Å). The gold–phosphine bond lengths (2.282–2.305 Å) are in the range normally bound for platinum–gold clusters, while the Au–Cl distances (2.339–2.388 Å) are relatively long compared to those of linear coordinated Au–Cl complexes (2.26 Å in PPh_3AuCl).[15] These long distances are

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Table IV. Effect of X on NMR and IR Data for $[Pt(CO)(AuPPh_3)_7(AuX)]^+$ (a) and $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$ (b)

		^{31}P NMR					
X	electronegativity of X[18]	δ(AuP), ppm		δ(PtP), ppm	$^2J(^{195}Pt-^{31}P)$, Hz		IR ν_{CO}, cm^{-1}
		a	b	b	a	b	a
PPh_3	2.0	51.3	47.4	61.0	391.2	409.0	1940
I^-	2.2	51.6	46.6	55.2	384.1	379.0	1948
Br^-	2.7	51.7	46.6	54.2	383.9	378.0	1949
OR^-	2.8[a]	52.3			379.2		1966
Cl^-	2.8	52.4	46.7	55.0	379.1	374.0	1949
^tBuNC		52.8			373.0		1951
^iPrNC		53.2			372.3		1954

[a] R = H.

in agreement with the low Au–Cl frequency (260 cm^{-1}) found in the IR spectrum (310–349 cm^{-1} for Au^ICl complexes).[16]

The composition of $[Pt(PPh_3)(AuPPh_3)_6(AuX)_3]$ suggests that it could be prepared by addition of three Au–X groups to $[Pt(PPh_3)(AuPPh_3)_6]$. This latter cluster can be obtained by the electrochemical reduction of $[Pt(PPh_3)(AuPPh_3)_6]^{2+}$.[17] The reaction of $[Pt(PPh_3)(AuPPh_3)_6]$ with AuX, however, results in fragmentation and oxidation of the cluster and the formation of gold metal.

Reaction of 18-Electron Clusters with X^- (X = I, Br, Cl, OR). The reaction of $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ and I^- leads to the formation of $[Pt(CO)(AuPPh_3)_7(AuI)](NO_3)$ in 95% yield.

$$[Pt(CO)(AuPPh_3)_8](NO_3)_2 + I^- \rightarrow [Pt(CO)(AuPPh_3)_7(AuI)](NO_3) + PPh_3 + NO_3^-$$

The elemental analysis is in agreement with this composition. The $^{31}P\{^1H\}$ NMR spectrum shows only one phosphine site and a Pt–P coupling of 384.1 Hz, which is in the range of $^2J(^{195}Pt-^{31}P)$ couplings. The ^{195}Pt NMR spectrum clearly shows an octet, so it can be concluded that there are seven $AuPPh_3$ groups bonded to Pt. The NMR data of $[Pt(^{13}CO)(AuPPh_3)_7(AuI)](NO_3)$ show the presence of one CO group bonded to Pt. The presence of one free NO_3^- is indicated by elemental analysis and by the existence of a PF_6^- salt in which only one PF_6 is present. All data indicate the presence of coordinated I^-, most probably attached to gold.

$[Pt(CO)(AuPPh_3)_7(AuBr)](NO_3)$ and $[Pt(CO)(AuPPh_3)_7(AuCl)](NO_3)$ are formed in nearly 100% yield from the reactions of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with Bu_4NBr and Bu_4NCl, respectively. The synthetic route and the NMR and IR data compared with those of $[Pt(CO)(AuPPh_3)_7(AuI)](NO_3)$ (see Table IV) are in agreement with the formulations $[Pt(CO)(AuPPh_3)_7(AuBr)]^+$ and $[Pt(CO)(AuPPh_3)_7(AuCl)]^+$ as the cluster cations. $[Pt(CO)(AuPPh_3)_7(AuCl)]^+$ reacts with I^- to form $[Pt(CO)(AuPPh_3)_7(AuI)]^+$. The hard Cl^- is substituted by the soft I^- ligand. This is also shown in the reaction of $AuPPh_3Cl$ with I^- that leads to the formation of $AuPPh_3I$. The reverse reactions do not occur. In the reaction of $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ with an excess of KOH in methanol $[Pt(CO)(AuPPh_3)_7(AuOR)](OR)$ is formed. The intensities of the Pt satellites in the ^{31}P NMR spectrum and the existence of an octet in the ^{195}Pt NMR spectrum indicate the presence of one Pt atom and seven $AuPPh_3$ groups. In the IR spectrum no characteristic frequencies of NO_3^-, OCH_3^-, or OH^- were found. The CO frequency is raised from 1940 cm^{-1} in $[Pt(CO)(AuPPh_3)_8]^{2+}$ to 1966 cm^{-1} in $[Pt(CO)(AuPPh_3)_7(AuOR)]^+$, probably due to the more electronegative OR^- with regard to PPh_3.[18] The synthetic route, the IR data, and the NMR data indicate that the cluster is closely related to $[Pt(CO)(AuPPh_3)_7(AuX)]^+$ (X = Cl, Br, I) (see Table IV). This is also supported by its reaction with I^- that leads to the formation of $[Pt(CO)(AuPPh_3)_7(AuI)]^+$. Therefore, we assume that the cluster is $[Pt(CO)(AuPPh_3)_7(AuOR)](OR)$, where R is either CH_3 or H. Due to impurities in the sample neither elemental analysis nor IR data could distinguish between these two possibilities. ^1H NMR spectra in the region of OH and OCH_3 were not decisive due to the presence of very broad lines.

In the reaction of $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ with 1 equiv of X^- (X = I, Br, Cl) $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$ is formed. From the IR spectrum it is concluded that NO_3^- is the counterion, which can be replaced by PF_6^-. ICP analysis shows the presence of one Pt, seven Au, and seven PPh_3 groups. The intensities of the different isotopomers in the ^{31}P, ^{195}Pt, and ^1H NMR spectra as well as the coupling constants indicate the presence of one Pt atom, and one PPh_3 group coordinated to this Pt atom ($^1J(^{195}Pt-^{31}P)$ = 2735 Hz), a Pt–H bond ($^1J(^{195}Pt-^1H)$ = 606 Hz), and six $AuPPh_3$ groups attached to Pt. The NMR data, collected in Table IV, clearly show a dependence of the halide used, indicating the halide to be bonded in the clusters, attached to the seventh gold atom. So the cluster cation can be formulated as $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$. This conclusion is supported by the reactions of $AuPPh_3I$ and $AuPPh_3Cl$ with $[Pt(H)(PPh_3)(AuPPh_3)_6]^+$ that lead to the formation of $[Pt(H)(PPh_3)(AuPPh_3)_6(AuI)]^+$ and $[Pt(H)(PPh_3)(AuPPh_3)_6(AuCl)]^+$, respectively.

$$[Pt(H)(PPh_3)(AuPPh_3)_6]^+ + AuPPh_3X \rightarrow [Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+ + PPh_3$$

In contrast with the reactions of $[Pt(CO)(AuPPh_3)_8]^{2+}$ and $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ with halides that lead to nearly complete conversion into $[Pt(CO)(AuPPh_3)_7(AuX)]^+$ and $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$, respectively, the reactions of $[Pt(H)(AuPPh_3)_8]^+$ and $[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$ with halides give fragmentation and complex reaction products. From the NMR data it can be concluded that in the reaction of $[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$ with I^- Ag^+ is eliminated and $[Pt(CO)(AuPPh_3)_7(AuI)]^+$ is formed.

Discussion

The formation of $[Pt(PPh_3)(AuPPh_3)_6(AuX)_3]$ from $[Pt(AuPPh_3)_8]^{2+}$ and X^- must occur in several steps. We suggest a mechanism, proposed on the ability of the 16-electron systems to accept 2 more electrons. First, a nucleophilic addition of X^- will occur, followed by elimination of PPh_3AuX and the formation of the intermediate $[Pt(AuPPh_3)_7]^+$. The next step is an addition of PPh_3 and the formation of the 18-electron system $[Pt(PPh_3)(AuPPh_3)_7]^+$. This cluster compound was also isolated from the reaction mixture and characterized. In the reactions of 18-electron clusters with halides one PPh_3 group on gold is substituted by X, so we propose the formation of $[Pt(PPh_3)(AuPPh_3)_6(AuX)]$ from $[Pt(PPh_3)(AuPPh_3)_7]^+$ and X^-. Adding two more AuX groups leads to $[Pt(PPh_3)(AuPPh_3)_6(AuX)_3]$. PPh_3 and AuX are formed by partial dissociation of PPh_3AuX.

$$[Pt(AuPPh_3)_8]^{2+} + X^- \rightarrow [Pt(AuPPh_3)_7]^+ + PPh_3AuX$$

$$[Pt(AuPPh_3)_7]^+ + PPh_3 \rightarrow [Pt(PPh_3)(AuPPh_3)_7]^+$$

$$[Pt(PPh_3)(AuPPh_3)_7]^+ + X^- \rightarrow [Pt(PPh_3)(AuPPh_3)_6(AuX)] + PPh_3$$

$$[Pt(PPh_3)(AuPPh_3)_6(AuX)] + 2AuX \rightarrow [Pt(PPh_3)(AuPPh_3)_6(AuX)_3]$$

The analogous reaction of $[Au(AuPPh_3)_8]^{3+}$ was investigated thoroughly in the past. Vollenbroek et al.[19,20] reported the fragmentation and growth of $[Au(AuPPh_3)_8]^{3+}$ to $[Au(AuPPh_3)_7(AuX)_3]$ or $[Au(AuPPh_3)_8(AuX)_2]^+$ when X is SCN^-

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and Cl$^-$, respectively. In both reactions $[Au(PPh_3)(AuPPh_3)_7]^{2+}$ is an intermediate and a possible mechanism is

$$[Au(AuPPh_3)_8]^{3+} \rightleftarrows [Au(AuPPh_3)_7]^{2+} + AuPPh_3^+$$

$$[Au(AuPPh_3)_7]^{2+} + PPh_3 \rightleftarrows [Au(PPh_3)(AuPPh_3)_7]^{2+}$$

$$[Au(PPh_3)(AuPPh_3)_7]^{2+} + X^- + 2e^- \rightarrow [Au_{11}] + \text{unidentified products}$$

To complete the number of electrons to 18, a reaction step leading to the Au_{11} cluster must be a reduction with 2 electrons. In fact, for the gold cluster compounds, disproportionation reactions are well-known.[21] The fragments can easily be oxidized. In platinum-gold cluster chemistry no such reactions are known and a phosphine addition to the central platinum completes the 18-electron configuration.

The complexity of the ^{31}P NMR spectrum may be due to a rigidity of the cluster compound $[Pt(PPh_3)(AuPPh_3)_6(AuX)_3]$. Normally, in solution at room temperature, the gold-phosphine sites in cluster compounds show a fluxional behavior, equilibrating all gold-phosphine sites so they yield a single peak in the ^{31}P NMR spectrum.[22,23] Another possible explanation for the complexity of the spectrum is the presence of different isomers. Because of the low solubility of the compound, it was not possible to use different NMR techniques (VT-NMR, 2D-COSY, ^{195}Pt) to establish the real cause for the complexity.

The $[Pt(CO)(AuPPh_3)_8]^{2+}$ and the $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ clusters are 18-electron systems, and so the coordination of an additional nucleophilic ligand to the platinum center is not possible. It turned out that substitution is limited to the Au-bonded phosphines; the Pt-bonded PPh_3 and CO are inert to substitution.

The reactions of $[Pt(CO)(AuPPh_3)_8]^{2+}$ and $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ with halides give $[Pt(CO)(AuPPh_3)_7(AuX)]^+$ and $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$, respectively, in high yields. Substitution is limited to a single PPh_3, even with a large excess of halide. This limit is also found in the substitution reactions with isocyanides.[2] An explanation could be the steric strain present in a system with eight PPh_3 groups and one CO. When one PPh_3 is replaced by a smaller ligand, the strain is removed and no further substitution will take place. The reaction of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with two CN$^-$ ions in which $[Pt(CO)(AuPPh_3)_6(AuCN)_2]$ is formed is probably due to the high affinity of CN$^-$ for gold. Electronic properties of the incoming ligand will influence the chemical shifts and coupling constants of the ^{31}P NMR spectrum and the CO frequencies in the IR spectra (Table IV). A ligand with a higher electronegativity gives a lower electron density on the cluster, less shielding of the phosphorus atoms, and a slight increase of the chemical shift of the phosphorus atoms. Parallel goes a decrease of the $^2J(^{195}Pt-^{31}P)$ coupling constants, suggesting weaker Pt-Au-P bonding, and an increase of the CO frequency. For the $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$ clusters, the same trend is found for the $^2J(^{195}Pt-^{31}P)$ coupling constants (Table IV). However, the chemical shifts show an opposite trend. This phenomenon is also found for Ag, Au, Hg, and Pt complexes[24-28] and is summarized by Bos.[29] The reactions of $[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$ and $[Pt(H)(AuPPh_3)_8]^+$ with halides do not lead to simple substitution but to a decomposition of the starting clusters and complex reaction mixtures.

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Supplementary Material Available: Listings of complete crystallographic data and data collection parameters, additional temperature factors, fractional positional parameters, thermal parameters, and bond distances and angles (14 pages); a listing of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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Low-Temperature Synthesis of Vanadium Sulfides

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The ambient-temperature reactions between VCl_4 and the sulfurizing agents $[(CH_3)_3Si]_2S$, $[(CH_3)_3C]_2S_2$, $[(CH_3)_3C]_2S$, and H_2S have been studied. We have observed that VCl_4 reacts differently from other transition-metal halides when sulfurized at low temperature. Indeed, the low-temperature sulfurization of VCl_4 almost always yields amorphous VS_4, with the formation of S-S bonds. The only exception we have observed is the reaction of VCl_4 with Li_2S, which yields Li_xVS_2.

Introduction

Layered transition-metal disulfides are of great interest due to their electronic properties, catalytic behavior, and insertability.[1,2] Conventionally, most of the transition-metal disulfides are prepared by stoichiometric reactions of the elements above 500 °C.[3-5]

In the group 4 and 5 transition-metal sulfides MS_2, VS_2 is the only compound that has not been prepared by direct combination of the elements. In the vanadium-sulfur system, V_5S_8 appears to be the most sulfur-rich vanadium sulfide that can be prepared by reaction between the elements.[6,7] Chianelli and Dines[8] at-

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