solution, the concentration of MeI is insufficient to drive the equilibrium to $Rh(Me)(I)_2(CO)(PPh_3)_2$ and *trans*-$Rh(CO)(PPh_3)_2I$ is observed as the rhodium product. The failure of $Ph_2CHC(O)Cl$ to add to *trans*-$Rh(CO)(PPh_3)_2Cl$ may also indicate the greater stability of Rh(I) over that of Rh(III), although in this case the lack of solubility of *trans*-$Rh(CO)(PPh_3)_2Cl$ may also be a significant factor.

The formation of ethers from reactions of methyl iodide with *trans*-$PhORh(CO)(PPh_3)_2$ is a significant addition to carbon–oxygen bond-forming reactions.

Acknowledgment. We acknowlege the National Science Foundation (Grant No. CHE-8709563) for support of this research and thank Professor Bruce M. Foxman of Brandeis University for providing us with a copy of his IBM PC version of ORTEP-II.[32]

Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a list of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

(30) Douek, J. C.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 2604.
(31) Franks, S.; Hartley, F. R.; Chipperfield, J. R. *Inorg. Chem.* **1981**, *20*, 3238.
(32) Johnson, C. K. "ORTEP-II: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations"; Oak Ridge National Laboratory, Oak Ridge, TN, 1976. IBM PC version by B. M. Foxman, Brandeis University, Waltham, MA, 1987.

Synthesis of Extremely Stable Alkyl and Hydride Complexes of the Type $(R_2NCS_2)Pt(PEt_3)R$

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Received December 6, 1988

The reaction of $(R_2NCS_2)Pt(PEt_3)Cl$ (R = Me, Et), prepared from $[Pt(PEt_3)Cl_2]_2$ and $Na(R_2NCS_2)$, with alkyllithium or Grignard reagents yields $(R_2NCS_2)Pt(PEt_3)$(alkyl) (alkyl = Me, *n*-Pr, *i*-Pr, *n*-Bu, *sec*-Bu, *i*-Bu, *t*-Bu) complexes. These new alkylplatinum complexes are very stable and can be heated in solution at 100 °C for extended periods without decomposition. The reaction of $(R_2NCS_2)Pt(PEt_3)Cl$ with $NaBH_4$ yields the stable complexes $(R_2NCS_2)Pt(PEt_3)H$, which decompose only slowly at 110 °C. This hydride (R = Me) does not react with ethylene or phenylacetylene but will react with $MeO_2CC{\equiv}CCO_2Me$ to yield a mixture of the *E* and *Z* isomers of $(Me_2NCS_2)Pt(PEt_3)(\eta^1\text{-}C(CO_2Me){=}C(H)CO_2Me)$. The reaction of $(R_2NCS_2)Pt(PEt_3)Cl$ with $AgBF_4$ and ethylene yields $[(R_2NCS_2)Pt(PEt_3)(C_2H_4)]BF_4$, but these complexes are very unstable, decomposing rapidly in the absence of ethylene. The complexes $(Me_2NCS_2)PtLCl$ (L = CO, C_2H_4) are prepared by mixing the L ligand with $[Pt(Me_2NCS_2)Cl]_2$.

Introduction

The investigation of the synthesis and reactivity of alkylmetal complexes is central to the understanding of many processes catalyzed by transition metals.[1] An important example of a catalytic process involving alkylmetal intermediates is the hydroformylation reaction.[2] Continuing our interest in alkylmetal complexes, we desired flexible and direct synthetic routes to neutral complexes of platinum that contain one alkyl ligand of the general formula (A-A)PtL(alkyl), where A-A is a bidentate, monoanionic ligand and L is a neutral, two-electron-donor ligand. A number of (A-A)PtLX (X = halide) type starting materials are known, as are a few (A-A)PtL(alkyl) complexes.[3] We anticipated that this class of compounds, containing classic coordination chemistry ligands, would yield stable new alkylmetal complexes useful for a number of desired model studies relating to the hydroformylation reaction.

Described here are efforts directed at the synthesis of these (A-A)PtL(alkyl) complexes, where $(A\text{-}A)^-$ is the dialkyldithiocarbamato ligand and L is PEt_3. We report that dialkyldithiocarbamato complexes, $(R_2NCS_2)Pt(PEt_3)$(alkyl) (R = Me, Et), are readily synthesized for a wide variety of alkyl groups and are extremely stable. The extremely stable hydride complexes $(R_2NCS_2)Pt(PEt_3)H$ are readily prepared and react (R = Me) with $MeO_2CC{\equiv}CCO_2Me$ to yield a mixture of the *E* and *Z* isomers of $(Me_2NCS_2)Pt(PEt_3)[\eta^1\text{-}C(CO_2Me){=}C(H)CO_2Me]$. We also report the synthesis of $[(R_2NCS_2)Pt(PEt_3)(C_2H_4)]BF_4$ and $(R_2NCS_2)PtLCl$ (L = CO, C_2H_4) complexes.

(1) Collman, J. P.; Hegedus, L.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.
(2) (a) Henrici-Olive, G.; Olive, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer-Verlag: New York, 1984. (b) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. (c) Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, Chapter 50.3.
(3) Roundhill, D. M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 5, Chapter 52.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere with use of either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. The ^1H and ^{31}P NMR spectra were recorded on a Bruker AM300 spectrometer using a 5-mm broad-band probe. An IBM NR-80 spectrometer was used to obtain ^{13}C NMR spectra. ^1H and ^{31}P NMR chemical shifts are reported in ppm versus TMS and H_3PO_4, respectively. The triethylphosphine proton resonances are seen

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as a doublet of quartets for the CH_2 resonance (J_{HP} = 10 Hz, J_{HH} = 8 Hz) and a doublet of triplets for the CH_3 resonance (J_{HP} = 17 Hz, J_{HH} = 8 Hz). These coupling constants are not reported separately for each compound. Carbon-13 NMR chemical shifts are reported vs TMS with $CDCl_3$ as the internal standard ($CDCl_3$ resonance at 77.00 ppm). High-resolution mass spectra were run as solids and fast atom bombardment mass spectra in a 3-nitrobenzyl alcohol matrix on a VG 70SQ spectrometer; low-resolution spectra were recorded on a Finnigan 4521 GC–mass spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by Robertson Laboratory, Inc. $Pt_2Cl_4(PEt_3)_2$[4] and $[Pt(Me_2NCS_2)Cl]_2$[5] were prepared by the published methods. Methyl-, *n*-butyl-, *sec*-butyl-, *tert*-butyl-, and phenyllithium and isobutyl-, *n*-propyl-, and isopropylmagnesium chlorides were purchased from Aldrich Chemical Co. and used as received.

(Dimethyldithiocarbamato)chloro(triethylphosphine)-platinum(II), $(Me_2NCS_2)Pt(PEt_3)Cl$. $Pt_2Cl_4(PEt_3)_2$ (0.10 g, 0.13 mmol) and $Na(Me_2NCS_2)\cdot 2H_2O$ (0.047 g, 0.26 mmol) were combined in a 50-mL round-bottomed flask. CH_2Cl_2 (10 mL) was added to the solids. The reaction mixture was stirred at room temperature for 3 h. The solution was filtered and the solvent removed under vacuum. The product was a yellow solid (0.12 g, 0.26 mmol, 100%). ^1H NMR (δ, $CDCl_3$): 3.23, 3.20 (s, s; 3, 3; NMe_2); 1.79 (6, PCH_2CH_3); 1.13 (9, PCH_2CH_3). ^{31}P NMR (δ, $CDCl_3$): 6.76 (J_{PPt} = 3520 Hz). The mass spectrum shows clusters at *m/e* 469 (M^+) and 432 (M^+ – Cl). Anal. Calcd for $C_9H_{21}ClNPPtS_2$: C, 23.08; H, 4.49. Found: C, 23.02; H, 4.28.

(Dimethyldithiocarbamato)hydrido(triethylphosphine)-platinum(II), $(Me_2NCS_2)Pt(PEt_3)H$. $(Me_2NCS_2)Pt(PEt_3)Cl$ (0.12 g, 0.26 mmol) was dissolved in THF (5 mL). The solution was cooled to 0 °C. $NaBH_4$ (0.020 g, 0.52 mmol) was added. The reaction mixture was allowed to warm up to room temperature (2 h). The solvent was removed under vacuum. The product was extracted with benzene to yield a yellow oil (0.11 g, 0.25 mmol, 97%). ^1H NMR (δ, $CDCl_3$): 3.23, 3.21 (s, s; 3, 3; NMe_2); 1.76 (6, PCH_2CH_3); 1.07 (9, PCH_2CH_3); –15.3 (d, 1, J_{HPt} = 1301 Hz, J_{HP} = 25 Hz, PtH). ^{31}P NMR (δ, $CDCl_3$): 13.56 (J_{PPt} = 3629 Hz). The high-resolution mass spectrum shows M^+ (*m/e*): calcd for $C_9H_{22}NP^{194}PtS_2$, 433.0558; found, 433.0544. Anal. Calcd for $C_9H_{22}NPPtS_2$: C, 24.88; H, 5.07. Found: C, 25.18; H, 5.07.

(Dimethyldithiocarbamato)methyl(triethylphosphine)-platinum(II), $(Me_2NCS_2)Pt(PEt_3)(\eta^1\text{-}CH_3)$. $(Me_2NCS_2)Pt(PEt_3)Cl$ (0.12 g, 0.26 mmol) was dissolved in THF (5 mL). The solution was cooled to –78 °C, and methyllithium (0.18 mL, 0.26 mmol, 1.35 M) was added. The reaction mixture was allowed to warm up to room temperature (4 h), and the solvent was removed under vacuum. The product was extracted with benzene to yield a golden brown solid (0.10 g, 0.22 mmol, 86%). ^1H NMR (δ, $CDCl_3$): 3.23, 3.22 (s, s; 3, 3; NMe_2); 1.75 (6, PCH_2CH_3); 1.09 (9, PCH_2CH_3); 0.49 (d, 3, J_{HPt} = 78 Hz, J_{HP} = 4 Hz, Pt–CH_3). ^{31}P NMR (δ, $CDCl_3$): 8.12 (J_{PPt} = 3894 Hz). The high-resolution mass spectrum shows M^+ (*m/e*): calcd for $C_{10}H_{24}NP^{195}PtS_2$ 448.0736; found, 448.0740. Anal. Calcd for $C_{10}H_{24}NPPtS_2$: C, 26.78; H, 5.39. Found: C, 26.95; H, 5.42.

(Dimethyldithiocarbamato)-*n*-butyl(triethylphosphine)platinum(II), $(Me_2NCS_2)Pt(PEt_3)(\eta^1\text{-}CH_2CH_2CH_2CH_3)$. This complex is prepared as indicated above for the methyl analogue in 84% yield. ^1H NMR (δ, $CDCl_3$): 3.27, 3.24 (s, s; 3, 3; NMe_2); 1.74 (6, PCH_2CH_3); 1.41, 1.30 (m, m; 6; $PtCH_2CH_2CH_2CH_3$); 1.10 (9, PCH_2CH_3); 0.83 (t, 3, J = 7 Hz, $PtCH_2CH_2CH_2CH_3$). ^{31}P NMR (δ, $CDCl_3$): 8.40 (J_{PPt} = 4022 Hz). Anal. Calcd for $C_{13}H_{30}NPPtS_2$: C, 31.83; H, 6.17. Found: C, 31.90; H, 5.91.

(Dimethyldithiocarbamato)-*sec*-butyl(triethylphosphine)platinum(II), $(Me_2NCS_2)Pt(PEt_3)[\eta^1\text{-}CH(CH_3)CH_2CH_3]$. This complex is prepared as indicated above for the methyl analogue in 85% yield. ^1H NMR (δ, $CDCl_3$): 3.27, 3.24 (s, s; 3, 3; NMe_2); 1.73 (6, PCH_2CH_3); 1.6 (m, 3, $CHCH_2$); 1.17 (d, 3, J = 7 Hz, $CHCH_3$); 1.11 (9, PCH_2CH_3); 0.97 (t, 3, J = 7 Hz, $PtCHCH_2CH_3$). ^{31}P NMR (δ, $CDCl_3$): 7.95 (J_{PPt} = 4190 Hz). The high-resolution mass spectrum shows M^+ (*m/e*): calcd for $C_{13}H_{30}NP^{194}PtS_2$, 489.1184; found, 489.1171.

(Dimethyldithiocarbamato)isobutyl(triethylphosphine)-platinum(II), $(Me_2NCS_2)Pt(PEt_3)(\eta^1\text{-}CH_2CH(CH_3)_2)$. $(Me_2NCS_2)Pt(PEt_3)Cl$ (0.13 g, 0.28 mmol) was dissolved in THF (25 mL) and cooled to –78 °C, and isobutylmagnesium chloride (0.28 mL, 0.56 mmol, 2.0 M) was added. The reaction mixture was allowed to warm up to room temperature (2 h) and was then heated at reflux for 1 h. The solvent was removed, and the product was extracted with benzene to yield a yellow solid (0.050 g, 0.10 mmol, 36%). ^1H NMR (δ, $CDCl_3$): 3.27, 3.25 (s, s; 3, 3; NMe_2); 1.75 (6, PCH_2CH_3); 1.31 (3; d of d; J_{HH} = 7 Hz, J_{HP} = 5 Hz; $PtCH_2$); 1.11 (9, PCH_2CH_3); 0.94 (6, d, J = 7 Hz, $CH(CH_3)_2$); methine hydrogen atom not clearly assigned. ^{31}P NMR (δ, $CDCl_3$): 8.45 (J_{PPt} = 4028 Hz). The high-resolution mass spectrum shows M^+ (*m/e*): calcd for $C_{13}H_{30}NP^{194}PtS_2$, 489.1184; found, 489.1162.

(Dimethyldithiocarbamato)-*tert*-butyl(triethylphosphine)platinum(II), $(Me_2NCS_2)Pt(PEt_3)[\eta^1\text{-}C(CH_3)_3]$. $(Me_2NCS_2)Pt(PEt_3)Cl$ (0.10 g, 0.21 mmol) was dissolved in THF (10 mL) and cooled to –78 °C. A solution of *tert*-butyllithium (0.15 mL, 0.26 mmol, 1.7 M) in hexane (10 mL) was cooled to –78 °C and added dropwise to the THF solution. The reaction mixture was allowed to warm up to room temperature (4 h), and the solvent was removed under vacuum. The product was extracted with benzene and chromatographed on a short silica column. The product was a golden brown oil (0.033 g, 0.068 mmol, 32%). ^1H NMR (δ, $CDCl_3$): 3.27, 3.23 (s, s; 3, 3; NMe_2); 1.8 (6, PCH_2CH_3); 1.14 (d, 9, J_{HP} = 1 Hz, J_{HPt} = 52 Hz, $C(CH_3)_3$); 1.1 (9, PCH_2CH_3). ^{31}P NMR (δ, $CDCl_3$): 2.73 (J_{PPt} = 4355 Hz). Anal. Calcd for $C_{13}H_{30}NPPtS_2$: C, 31.83; H, 6.17. Found: C, 32.18; H, 6.32.

(Dimethyldithiocarbamato)(ethylene)(triethylphosphine)platinum(II) Tetrafluoroborate, $[(Me_2NCS_2)Pt(PEt_3)(\eta^2\text{-}CH_2{=}CH_2)]BF_4$. $(Me_2NCS_2)Pt(PEt_3)Cl$ (0.12 g, 0.26 mmol) and $AgBF_4$ (0.050 g, 0.26 mmol) were placed in a 50-mL round-bottomed flask. In a separate flask, CH_2Cl_2 (20 mL) was saturated with ethylene. This ethylene solution was cannulated into the flask containing the solids. Ethylene was bubbled into the reaction mixture (2 h). The system was then closed off, and the reaction mixture was stirred (16 h). The solution was filtered and the solvent removed. The product was a pale yellow solid. The compound is very unstable and decomposes rapidly. ^1H NMR (δ, $CDCl_3$): 4.69 (d, 4, J_{HPt} = 60 Hz, J_{HP} = 3 Hz, $CH_2{=}CH_2$); 3.42, 3.40 (s, s; 3, 3; NMe_2); 1.92 (6, PCH_2CH_3); 1.19 (9, PCH_2CH_3). ^{31}P NMR (δ, $CDCl_3$): 9.68 (J_{PPt} = 2983 Hz). The reaction chemistry was carried out immediately after solvent removal. Reaction with $Ph_2Cu(CN)Li_2$ or PhLi (1 equiv) in THF at –78 °C yielded a yellow solid, $(Me_2NCS_2)Pt(PEt_3)Ph$. ^1H NMR (δ, $CDCl_3$): 7.49 (d, 2, *o*-Ph); 6.91 (t, 2, *m*-Ph); 6.80 (t, 1, *p*-Ph); 3.24, 3.20 (s, s; 3, 3; NMe_2); 1.61 (6, PCH_2CH_3); 1.09 (9, PCH_2CH_3). ^{31}P NMR (δ, $CDCl_3$): 6.33 (J_{PPt} = 3827 Hz). The mass spectrum shows a cluster at *m/e* 510 (M^+).

(Diethyldithiocarbamato)chloro(triethylphosphine)-platinum(II), $(Et_2NCS_2)Pt(PEt_3)Cl$. Method A. $Pt_2Cl_4(PEt_3)_2$ (0.100 g, 0.13 mmol) and $Na(Et_2NCS_2)\cdot 3H_2O$ (0.054 g, 0.26 mmol) were combined in the manner outlined above for the dimethyldithiocarbamato analogue. The product was a yellow solid (0.13 g, 0.26 mmol, 100%).

Method B. $Pt(PEt_3)_2Cl_2$ (1.01 g, 2.01 mmol) and $Pt(Et_2NCS_2)_2$ (1.00 g, 2.03 mmol) were combined in a 100-mL round-bottomed flask. Toluene (50 mL) was added. The reaction mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature and filtered. Hexane (100 mL) was added to the filtrate. Crystallization of the product was induced by passing a stream of N_2 over the solution until the volume was reduced by 50%, yielding 0.90 g (1.8 mmol, 45%) of yellow crystals. An additional 0.61 g (1.2 mmol, 30%) can be obtained by further evaporation of the filtrate. ^1H NMR (δ, $CDCl_3$): 3.60, 3.53 (q, q; 2, 2; J = 7 Hz; NCH_2CH_3); 1.77 (6, PCH_2CH_3); 1.23, 1.22 (t, t; 3, 3; J = 7 Hz; NCH_2CH_3); 1.12 (9, PCH_2CH_3). ^{31}P NMR (δ, $CDCl_3$): 6.70 (J_{PPt} = 3504 Hz). The high-resolution mass spectrum shows M^+ (*m/e*): calcd for $C_{11}H_{25}{}^{35}ClNP^{194}PtS_2$, 495.0467; found, 495.0481. Anal. Calcd for $C_{11}H_{25}NPPtS_2$: C, 26.59; H, 5.07. Found: C, 26.72; H, 5.01.

(Diethyldithiocarbamato)hydrido(triethylphosphine)-platinum(II), $(Et_2NCS_2)Pt(PEt_3)H$. This compound was

(4) Smithies, A. C.; Rycheck, M.; Orchin, M. *J. Organomet. Chem.* **1968**, *12*, 199.

(5) Faraglia, G.; Sindellari, L.; Trincia, L.; Furlani, A.; Scarcia, V. *Inorg. Chim. Acta* **1985**, *106*, 31.

prepared in 50% yield as described for the dimethyldithiocarbamato analogue. ^{1}H NMR (δ, $CDCl_3$): 3.62, 3.61 (q, q; 2, 2; J = 7 Hz; NCH_2CH_3); 1.76 (6, PCH_2CH_3); 1.24, 1.23 (t, t; 3, 3; J = 7 Hz; NCH_2CH_3); 1.06 (9, PCH_2CH_3); −15.2 (d, 1, J_{HPt} = 1292 Hz, J_{HP} = 24.8 Hz, PtH). ^{31}P NMR (δ, $CDCl_3$): 13.53 (J_{PPt} = 3606 Hz). The high-resolution mass spectrum shows M^+ (m/e): calcd for $C_{11}H_{26}NP^{194}PtS_2$, 461.0871; found, 461.0848. Anal. Calcd for $C_{11}H_{26}NPPtS_2$: C, 28.57; H, 5.63. Found: C, 28.37; H, 5.58.

(Diethyldithiocarbamato)methyl(triethylphosphine)platinum(II), $(Et_2NCS_2)Pt(PEt_3)(\eta^1\text{-}CH_3)$. $(Et_2NCS_2)Pt(PEt_3)Cl$ (0.11 g, 0.22 mmol) was dissolved in THF (5 mL). The solution was cooled to −78 °C, and methyllithium (0.16 mL, 0.22 mmol, 1.35 M) was added. The reaction mixture was allowed to warm up to room temperature (4 h), and the solvent was removed under vacuum. The product was extracted with benzene to yield a yellow solid (0.10 g, 0.21 mmol, 95%). ^{1}H NMR (δ, $CDCl_3$): 3.63 (q, 4, J = 7 Hz, NCH_2CH_3); 1.75 (6, PCH_2CH_3); 1.25, 1.23 (t, t; 3, 3; J = 7 Hz; NCH_2CH_3); 1.09 (9, PCH_2CH_3); 0.47 (d, 3, J_{HPt} = 77 Hz, J_{HP} = 4 Hz, Pt–CH_3). ^{31}P NMR (δ, $CDCl_3$): 7.96 (J_{PPt} = 3865 Hz). ^{13}C NMR (δ, $CDCl_3$): 44.4 (s, NCH_2CH_3); 16.0 (d, J_{CPt} = 50 Hz, J_{CP} = 35 Hz, PCH_2CH_3); 12.3 (s, NCH_2CH_3); 8.0 (d, J_{CPt} = 30 Hz, J_{CP} = 2 Hz, PCH_2CH_3); −18.5 (d, J_{CP} = 8 Hz, $PtCH_3$). The high-resolution mass spectrum shows M^+ and M^+ − Me (m/e): calcd for $C_{12}H_{28}NP^{194}PtS_2$, $C_{11}H_{25}NP^{194}PtS_2$, 475.1028, 460.0793; found, 475.1054, 460.0831. Anal. Calcd for $C_{12}H_{28}NPPtS_2$: C, 30.12; H, 5.90. Found: C, 30.40; H, 6.16.

(Diethyldithiocarbamato)-*n*-propyl(triethylphosphine)platinum(II), $(Et_2NCS_2)Pt(PEt_3)(\eta^1\text{-}CH_2CH_2CH_3)$. $(Et_2NCS_2)Pt(PEt_3)Cl$ (0.13 g, 0.26 mmol) was dissolved in THF (5 mL). The solution was cooled to −78 °C, and *n*-propylmagnesium chloride (0.13 mL, 0.26 mmol, 2.0 M) was added. The reaction mixture was allowed to warm up to room temperature (4 h), and the solvent was removed under vacuum. The product was extracted with benzene to yield a yellow solid (0.10 g, 76%). ^{1}H NMR (δ, $CDCl_3$): 3.26, 3.20 (q, q; 2, 2; J = 7 Hz; NCH_2CH_3); 1.46 (6, PCH_2CH_3); 1.37 (t, 3, J = 7 Hz, $PtCH_2CH_2CH_3$); 0.92 (9, PCH_2CH_3); 0.83 (m, 6, J = 7 Hz; NCH_2CH_3); methylene hydrogen atoms of the propyl group not clearly assigned. ^{31}P NMR (δ, C_6D_6): 8.22 (J_{PPt} = 4036 Hz). The high-resolution mass spectrum shows M^+ (m/e): calcd for $C_{14}H_{32}NP^{194}PtS_2$, 503.1341; found, 503.1342. Anal. Calcd for $C_{14}H_{32}NPPtS_2$: C, 33.32; H, 6.39. Found: C, 33.40; H, 6.25.

(Diethyldithiocarbamato)isopropyl(triethylphosphine)platinum(II), $(Et_2NCS_2)Pt(PEt_3)[\eta^1\text{-}CH(CH_3)_2]$. $(Et_2NCS_2)Pt(PEt_3)Cl$ (0.10 g, 0.20 mmol) was dissolved in THF (10 mL). The solution was cooled to −78 °C, and isopropylmagnesium chloride (0.15 mL, 0.30 mmol, 2.0 M) was added. The reaction mixture was allowed to warm up to room temperature (4 h), and the solvent was removed under vacuum. The product was extracted with benzene and chromatographed on a short silica column. The product was a yellow oil (0.040 g, 0.079 mmol, 40%). The product was a mixture of the isopropyl and *n*-propyl complexes (5:1). The analytical sample was obtained by dissolving the yellow oil in hexane and placing the solution in a −30 °C freezer overnight to yield yellow crystals. ^{1}H NMR (δ, $CDCl_3$): 3.26, 3.21 (q, q; 2, 2; J = 7 Hz; NCH_2CH_3); 1.81 (d, 6, J_{HH} = 7 Hz, J_{HPt} = 28 Hz, $CHCH_3$'s); 1.46 (6, PCH_2CH_3); 0.92 (9, PCH_2CH_3); 0.83 (m, 6, J = 7 Hz, NCH_2CH_3); methine hydrogen atom not clearly assigned. ^{31}P NMR (δ, C_6D_6): 8.73 (J_{PPt} = 4140 Hz). The high-resolution mass spectrum shows M^+ (m/e): calcd for $C_{14}H_{32}NP^{198}PtS_2$, 507.1393; found, 507.1359. Anal. Calcd for $C_{14}H_{32}NPPtS_2$: C, 33.32; H, 6.39. Found: C, 33.41; H, 6.41.

(Diethyldithiocarbamato)-*n*-butyl(triethylphosphine)platinum(II), $(Et_2NCS_2)Pt(PEt_3)(\eta^1\text{-}CH_2CH_2CH_2CH_3)$. This complex is prepared as indicated above for the methyl analogue in 96% yield. ^{1}H NMR (δ, $CDCl_3$): 3.63, 3.61 (q, q; 2, 2; J = 7 Hz; NCH_2CH_3); 1.69 (6, PCH_2CH_3); 1.22, 1.19 (t, t; 3, 3; J = 7 Hz; NCH_2CH_3); 1.05 (9, PCH_2CH_3); 0.77 (t, 3, J = 7 Hz, $PtCH_2CH_2CH_2CH_3$); remaining butyl resonances obscured by ethyl resonances from the other ligands. ^{31}P NMR (δ, $CDCl_3$): 8.16 (J_{PPt} = 3989 Hz). ^{13}C NMR (δ, $CDCl_3$): 211 (d, J_{CPt} = 64 Hz, J_{CP} = 3 Hz, S_2CN); 44.3 (s, NCH_2CH_3); 35.3 (s, J_{CPt} = 26 Hz, $CH_2CH_2CH_2CH_3$); 27.4 (s, J_{CPt} = 86 Hz, $CH_2CH_2CH_2CH_3$); 15.8 (d, J_{CPt} = 49 Hz, J_{CP} = 35 Hz, PCH_2CH_3); 14.0 (s, $CH_2CH_2CH_2CH_3$); 12.3 (s, NCH_2CH_3); 8.0 (d, J_{CPt} = 31 Hz, J_{CP} = 2 Hz, PCH_2CH_3); 2.7 (d, J_{CPt} = 669 Hz, J_{CP} = 7 Hz, $CH_2CH_2CH_2CH_3$). The high-resolution mass spectrum shows M^+ (m/e): calcd for $C_{15}H_{34}NP^{194}PtS_2$, 517.1497; found, 517.1492.

(Diethyldithiocarbamato)-*sec*-butyl(triethylphosphine)platinum(II), $(Et_2NCS_2)Pt(PEt_3)[\eta^1\text{-}CH(CH_3)CH_2CH_3]$. $(Et_2NCS_2)Pt(PEt_3)Cl$ (0.10 g, 0.20 mmol) was dissolved in THF (10 mL). The solution was cooled to −78 °C, and *sec*-butyllithium (0.31 mL, 0.22 mmol, 0.7 M) was added. The reaction mixture was allowed to warm up to room temperature (4 h), and the solvent was removed under vacuum. The product was extracted with hexane (3 × 4 mL). The hexane solution was reduced to 4 mL and placed in a −30 °C freezer overnight to yield yellow crystals (0.027 g, 0.052 mmol, 25%). An additional yield of crystals (0.046 g, 0.089 mmol, 45%) was obtained from the filtrate. ^{1}H NMR (δ, $CDCl_3$): 3.68 (q, 4, J = 7 Hz, NCH_2CH_3); 1.74 (6, PCH_2CH_3); 1.6 (m, 3, $CHCH_2$); 1.28, 1.23 (t, t; 3, 3; J = 7 Hz; NCH_2CH_3); 1.16 (3, d, J = 6 Hz, $CHCH_3$); 1.10 (9, PCH_2CH_3); 0.96 (t, 3, J = 7 Hz, $PtCHCH_2CH_3$). ^{31}P NMR (δ, $CDCl_3$): 7.97 (J_{PPt} = 4157 Hz). ^{13}C NMR (δ, $CDCl_3$): 44.6 (s, NCH_2CH_3); 34.1 (s, J_{CPt} = 25 Hz, $CHCH_2CH_3$); 24.1 (s, J_{CPt} = 28 Hz, $CHCH_3$); 15.5 (d, J_{CPt} = 49 Hz, J_{CP} = 35 Hz, PCH_2CH_3); 15.4 (s, $CHCH_2CH_3$); 12.4 (s, NCH_2CH_3); 8.0 (d, J_{CPt} = 31 Hz, J_{CP} = 2 Hz, PCH_2CH_3). The high-resolution mass spectrum shows M^+ (m/e): calcd for $C_{15}H_{34}NP^{194}PtS_2$, 517.1497; found, 517.1479. Anal. Calcd for $C_{15}H_{34}NPPtS_2$: C, 34.74; H, 6.61. Found: C, 34.60; H, 6.79.

(Diethyldithiocarbamato)-*tert*-butyl(triethylphosphine)platinum(II), $(Et_2NCS_2)Pt(PEt_3)[\eta^1\text{-}C(CH_3)_3]$. This complex is prepared as indicated above for the methyl analogue in 96% yield. ^{1}H NMR (δ, $CDCl_3$): 3.68, 3.65 (q, q; 2, 2; J = 7 Hz; NCH_2CH_3); 1.78 (6, PCH_2CH_3); 1.27, 1.24 (t, t; 3, 3; J = 7 Hz; NCH_2CH_3); 1.15 (s, 9, $C(CH_3)_3$); 1.12 (9, PCH_2CH_3). ^{31}P NMR (δ, $CDCl_3$): 2.58 (J_{PPt} = 4316 Hz). The high-resolution mass spectrum shows M^+ (m/e): calcd for $C_{15}H_{34}NP^{194}PtS_2$, 517.1497; found, 517.1482.

(Diethyldithiocarbamato)(ethylene)(triethylphosphine)platinum(II) Tetrafluoroborate, $[(Et_2NCS_2)Pt(PEt_3)(\eta^2\text{-}CH_2{=}CH_2)]BF_4$. $(Et_2NCS_2)Pt(PEt_3)Cl$ (0.13 g, 0.26 mmol) and $AgBF_4$ (0.05 g, 0.26 mmol) were placed in a 50-mL round-bottomed flask. In a separate flask, CH_2Cl_2 (20 mL) was saturated with ethylene. The solution was cannulated into the flask containing the solids. Ethylene was bubbled into the reaction mixture for the next 2 h. The system was then closed off, and the reaction mixture was stirred for 16 h. The solution was filtered and the solvent removed. The product was a yellow solid. The compound is very unstable and decomposes rapidly. ^{1}H NMR (δ, $CDCl_3$): 4.58 (d, 4, J_{HPt} = 57 Hz, J_{HP} = 3 Hz, C_2H_4); 3.74, 3.72 (q, q; 2, 2; J = 7 Hz; NCH_2CH_3); 1.93 (6, PCH_2CH_3); 1.36, 1.34 (t, t; 3, 3; J = 7 Hz; NCH_2CH_3); 1.07 (9, PCH_2CH_3).

(Dimethyldithiocarbamato)carbonylchloroplatinum(II), $(Me_2NCS_2)Pt(CO)Cl$. $[Pt(Me_2NCS_2)Cl]_2$ (0.19 g, 0.27 mmol) was placed in a 50-mL round-bottomed flask. CH_2Cl_2 (20 mL) was added to the solid. Carbon monoxide was slowly bubbled into the reaction mixture over the next 3 h. The solution was filtered, and the solvent was removed to yield a yellow solid (0.16 g, 0.42 mmol, 78%). ^{1}H NMR (δ, $CDCl_3$): 3.30, 3.27 (s, s; 3, 3; NMe_2). IR spectrum (CH_2Cl_2, cm^{-1}): 2093 (CO). The mass spectrum shows clusters at m/e 379 (M^+) and 351 (M^+ − CO). Anal. Calcd for $C_4H_6ClNOPtS_2$: C, 12.70; H, 1.59. Found: C, 13.32; H, 1.84.

(Dimethyldithiocarbamato)chloro(ethylene)platinum(II), $(Me_2NCS_2)Pt(\eta^2\text{-}CH_2{=}CH_2)Cl$. $[Pt(Me_2NCS_2)Cl]_2$ (0.17 g, 0.24 mmol) was placed in a 50-mL round-bottomed flask. CH_2Cl_2 (20 mL) was added to the solid. Ethylene was slowly bubbled into the reaction mixture over the next 3 h. The solution was filtered, and the solvent was removed to yield a yellow solid (0.06 g, 0.16 mmol, 67%). This complex slowly decomposes with time, making it impossible to obtain analytical figures. ^{1}H NMR (δ, $CDCl_3$): 4.53 (s, 4, J_{HPt} = 60 Hz, C_2H_4); 3.29, 3.22 (s, s; 3, 3; NMe_2). The FAB mass spectrum shows clusters at m/e 379 (M^+), 343 (M^+ − Cl), and 315 (M^+ − Cl − $CH_2{=}CH_2$).

Reaction of $MeO_2CC{\equiv}CCO_2Me$ and $(Me_2NCS_2)Pt(PEt_3)H$. $(Me_2NCS_2)Pt(PEt_3)H$ (0.11 g, 0.26 mmol) was dissolved in benzene (10 mL). The solution was cooled to −78 °C. Dimethyl acetylenedicarboxylate (35 μL, 0.26 mmol) was added. The reaction mixture was stirred at room temperature for 40 h. The solvent was removed under vacuum to yield an orange solid (0.07 g).

Analysis of the spectral data indicated the product was a mixture of four compounds. The two insertion products, $(Me_2NCS_2)Pt(PEt_3)[\eta^1\text{-}C(CO_2Me)=C(H)CO_2Me]$, were formed in the ratio 3:1 *E*:*Z*. The minor products, $(Me_2NCS_2)Pt(PEt_3)Ph$ and $MeO_2CC(H)=C(H)CO_2Me$, were identified by comparison to authentic samples. Spectral data for the *E* and *Z* isomers of $(Me_2NCS_2)Pt(PEt_3)[\eta^1\text{-}C(CO_2Me)=C(H)CO_2Me]$ follow. ^1H NMR (δ, $CDCl_3$): 6.60 (d, 1, J_{HPt} = 118 Hz, J_{HP} = 2 Hz, C=CH (*Z*)); 5.93 (d, 1, J_{HPt} = 88 Hz, J_{HP} = 1 Hz, C=CH (*E*)); 3.75, 3.58 (s, s; 3, 3; CO_2CH_3's (*E*)); 3.69, 3.67 (s, s; 3, 3; CO_2CH_3's (*Z*)); 3.22, 3.20 (s, s; 3, 3; NCH_3 (*E*)); 3.18, 3.17 (s, s; 3, 3; NCH_3 (*Z*)); 1.81 (6, PCH_2CH_3 (*E* + *Z*)); 1.09 (9, PCH_2CH_3 (*E* + *Z*)). ^{31}P NMR (δ, $CDCl_3$): 5.65 (J_{PPt} = 3540 Hz (*E*)); 3.79 (J_{PPt} = 3640 Hz (*Z*)). IR (CH_2Cl_2, cm^{-1}): 1707 (broad, CO). The high-resolution mass spectrum shows M^+ (*m*/*e*): calcd for $C_{15}H_{28}NO_4P^{194}PtS_2$, 575.0824; found, 575.0812.

Results and Discussion

The starting materials, $(R_2NCS_2)Pt(PEt_3)Cl$ (R = Me, Et), for the compounds reported here are prepared by the reaction of the platinum(II) dimer $Pt_2(PEt_3)_2Cl_4$ with the uninegative ligand as shown in eq 1. The yields of these

$$Pt_2(PEt_3)_2Cl_4 + 2(R_2NCS_2)^- \rightarrow 2(R_2NCS_2)Pt(PEt_3)Cl + 2Cl^- \quad (1)$$

compounds are essentially quantitative. A second method of preparation, used by others for the preparation of similar compounds,[6] was briefly investigated (eq 2). This

$$Pt(PEt_3)_2Cl_2 + Pt(R_2NCS_2)_2 \rightarrow 2(R_2NCS_2)Pt(PEt_3)Cl \quad (2)$$

method is also successful, but yields are lower than those using the method shown in eq 1.

The dithiocarbamate complexes react with alkyllithium reagents as shown in eq 3 to give the alkylplatinum complexes in almost quantitative yield. The propyl and iso-

$$(R_2NCS_2)Pt(PEt_3)Cl + R'Li \rightarrow (R_2NCS_2)Pt(PEt_3)R' + LiCl \quad (3)$$

R = Me, Et; R′ = Me, *n*-Bu, *sec*-Bu, *t*-Bu

butyl derivatives are prepared from Grignard reagents (eq 4). These complexes show the expected new resonances

$$(R_2NCS_2)Pt(PEt_3)Cl + R'MgCl \rightarrow (R_2NCS_2)Pt(PEt_3)R' + MgCl_2 \quad (4)$$

R = Et, R′ = *n*-Pr, *i*-Pr; R = Me, R′ = *i*-Bu

in ^1H NMR spectra for the alkyl ligand and are identifiable in ^{31}P NMR spectra by an increase in the phosphorus–platinum coupling constant from 3505–3520 Hz in the starting chloride to the range of 3865–4355 Hz. This coupling constant also shows a trend within the alkyl complexes. The values for primary alkyls are in the range 3865–4040 Hz (with the methyl complexes 100 Hz lower than the butyl or propyl), for secondary alkyls 4140–4190 Hz, and for the tertiary alkyls 4315–4355 Hz. These new alkyl compounds are extremely stable, can be heated to over 100 °C without decomposition, and will withstand chromatography on silica. Particularly notable is the stability of the tertiary alkyl complexes.[1] At temperatures above 100 °C, the alkyl ligand in the linear and branched isomers isomerizes to an equilibrium mixture of the two isomers. Also, in the preparation of the isopropyl compound, some of the *n*-propyl species is formed. Studies on these isomerization reactions will be reported separately.

A second method for the preparation of alkyl complexes in other systems is nucleophilic addition to η^2-alkene complexes.[7] This method is particularly useful for the introduction of heteroatom functional groups such as cyanide and thiols. The desired ethylene complexes are prepared by the reaction of the platinum–halide complexes with $AgBF_4$ and ethylene in a nondonor solvent (eq 5).

$$(R_2NCS_2)Pt(PEt_3)Cl + AgBF_4 + C_2H_4 \rightarrow [(R_2NCS_2)Pt(PEt_3)(\eta^2\text{-}CH_2{=}CH_2)]BF_4 + AgCl \quad (5)$$

These ethylene complexes are unstable, the ethylene ligand being lost as the solvent is removed under vacuum. In situ reactions with alkyllithium and alkylcuprate reagents immediately after preparation of the ethylene complexes lead to displacement of the ethylene ligand by the nucleophile. There is no indication of formation of the desired substituted alkylmetal complexes.

Another possible route to the preparation of alkylplatinum complexes containing functional groups involves the reaction of alkenes with platinum hydrides. The hydride complexes $(R_2NCS_2)Pt(PEt_3)H$ are prepared according to eq 6. These complexes are identified readily

$$(R_2NCS_2)Pt(PEt_3)Cl \xrightarrow{NaBH_4} (R_2NCS_2)Pt(PEt_3)H \quad (6)$$

by the hydride resonance in the ^1H NMR spectrum at ca. −15 ppm coupled to both platinum and phosphorus. Like the alkyl complexes, these hydride complexes show considerable thermal stability, decomposing only slowly at 110 °C in solution. The hydrides did not react with ethylene or phenylacetylene. However, the hydride complex (R = Me) does react with dimethyl acetylenedicarboxylate as shown in eq 7. The NMR data show that a mixture of

$$(Me_2NCS_2)Pt(PEt_3)H + MeO_2CC{\equiv}CCO_2Me \rightarrow (Me_2NCS_2)Pt(PEt_3)[\eta^1\text{-}C(CO_2Me){=}C(H)CO_2Me] \quad (7)$$

the *E* and *Z* isomers in a ratio of approximately 3:1 is obtained when the reaction is carried out in benzene. The stereochemistry of the alkenyl ligand can be assigned on the basis of the $^3J_{PtH}$ coupling constant and the position of the proton resonance.[8] The *Z* isomer has a $^3J_{HPt}$ value of 118 Hz, while for the *E* isomer the coupling constant is 88 Hz. In addition to the isomeric metal–alkenyl complexes, small amounts of $(Me_2NCS_2)Pt(PEt_3)Ph$ and $CH(CO_2Me){=}CH(CO_2Me)$ can be identified in the reaction mixture. Although no mechanistic studies have been carried out on this system, the presence of these compounds indicates that the reaction occurs by an electron-transfer process.[8c] For the same reaction carried out in methanol, the ratio of *E* and *Z* isomers that forms is 1:4. In addition to these products, ^1H NMR and mass spectral data indicate that oligomeric acetylene products, not observed in benzene, have also formed.

Another method that has been used to prepare platinum compounds of the type being investigated involves the reaction of a chloro-bridged dimer containing the bidentate ligand with the ligand L.[9] The chloride-bridged dimer $[Pt(Me_2NCS_2)Cl]_2$ reacts with both CO and ethylene to form $(Me_2NCS_2)Pt(CO)Cl$ and $(Me_2NCS_2)Pt(CH_2{=}CH_2)Cl$, as is outlined in eq 8. These complexes have not

(6) (a) Chan, L. T.; Chen, H.-W.; Fackler, J. P., Jr.; Masters, A. F.; Pan, W.-H. *Inorg. Chem.* **1982**, *21*, 4291. (b) Pan, W.-H.; Fackler, J. P., Jr.; Chen, H.-W. *Inorg. Chem.* **1981**, *20*, 856.

(7) (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) Reger, D. L.; McElligot, P. J. *J. Organomet. Chem.* **1981**, *216*, C12.

(8) (a) Mann, B. E.; Shaw, B. L.; Tucker, N. L. *J. Chem. Soc. A* **1971**, 2667. (b) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (c) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961.

(9) Fackler, J. P., Jr.; Lin, I. J. B.; Andrews, J. *Inorg. Chem.* **1977**, *16*, 450.

proven useful for the preparation of alkylplatinum complexes.

$$[Pt(Me_2NCS_2)Cl]_2 + 2L \rightarrow 2(Me_2NCS_2)PtLCl \quad (8)$$
$$L = CO, C_2H_4$$

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also partially supported by a grant from the University of South Carolina Venture Fund. The NSF (Grant CHE-8411172) and NIH (Grant RR-02425) have supplied funds to support NMR equipment, and the NIH (Grant RR-02849) has supplied funds to support mass spectrometry equipment.

Syntheses and NMR Spectra of $Co_3(CO)_9[\mu_3\text{-}CCHAr_2]$ Clusters Derived from DDT and Related Molecules: X-ray Crystal Structures of [[Bis(4-chlorophenyl)methyl]carbynyl]tricobalt Nonacarbonyl and of Its Bis(4-chloronaphthyl) Analogue

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Received December 20, 1988

The reaction of $Co_2(CO)_8$ with a series of 1,1,1-trichloro-2,2-bis(aryl)ethanes yields the corresponding $Co_3(CO)_9[\mu_3\text{-}CCHAr_2]$ tetrahedral clusters, where Ar = 4-chlorophenyl (**3**), 4-methoxyphenyl (**4**), or 4-chloronaphthyl (**6**). $Co_3(CO)_9[\mu_3\text{-}CCH(p\text{-}C_6H_4Cl)_2]$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ with a = 13.0834 (27) Å, b = 14.2224 (16) Å, c = 14.1649 (24) Å, β = 95.871 (15)°, V = 2621.9 (8) Å^3, and Z = 4; treatment of all 3434 unique data led to final values of R_F = 3.7% and R_{wF} = 3.3%. (R_F = 2.5% and R_{wF} = 3.0% for those 2781 data with $|F_o| > 6\sigma(|F_o|)$.) The chloronaphthyl cluster of $Co_3(CO)_9[\mu_3\text{-}CCH(C_{10}H_6Cl)_2]$ (**6**) crystallizes in the triclinic space group $P\bar{1}$ with a = 8.839 (3) Å, b = 12.156 (4) Å, c = 16.513 (5) Å, α = 105.974 (25)°, β = 92.280 (25)°, γ = 115.512 (22)°, V = 1513.57 (84) Å^3, and Z = 2; treatment of the 3620 unique data led to final values of R_F = 4.8% and R_{wF} = 5.3%. At −120 °C, the cobalt carbonyl ligands of the phenyl clusters **3** and **4** exhibit a 6:3 splitting in their ^{13}C NMR spectra; however, the naphthyl cluster **6** does not show this effect. These data are discussed in terms of the ability of the aryl groups to obstruct the fluxionality of the cobalt carbonyl ligands.

Introduction

The observed tendency of the carbynyl–tricobalt nonacarbonyl group to stabilize a positive charge in the α-position, as in the cluster $[(OC)_9Co_3(\mu_3\text{-}C{=}CR_2)]^+$, has been attributed to its ability to delocalize the charge onto the carbonyl ligands via the cobalts.[1] In order to compare the relative charge-stabilizing abilities of a C_6H_5 unit and a $(OC)_9Co_3(\mu_3\text{-}C)$ moiety, one needs to construct a molecule in which a phenyl ring and a carbynyl–nonacarbonyltricobalt unit are both attached to the same electron-deficient or electron-rich center. Therefore, it seemed a viable proposal to construct molecules in which one or more phenyl groups were bonded to a methynyl group situated in a position α to the nonacarbonyltricobalt moiety. By this means, one could remove the α-hydrogen either as a proton or as a hydride to prepare a cluster-stabilized anion or cation, respectively, and then determine the barrier to phenyl rotation in each case by variable-temperature NMR measurements. However, one needs a general route to clusters containing such arylmethyl- or diarylmethyl-capping functionalities. Nonacarbonyltricobalt clusters are most easily synthesized via the direct reaction of dicobalt octacarbonyl with an appropriate trichloromethyl-containing precursor. The acid-catalyzed reaction of arenes with trichloroacetaldehyde (chloral) is a very well-established process that leads to molecules of the type $Ar_2CH\text{–}CCl_3$.[2] Indeed, this is a general route to commercial pesticides such as 1,1,1-trichloro-2,2-bis(4-chlorophenyl)-ethane (DDT) **1** or the corresponding 4-methoxyphenyl compound (Methoxychlor) **2**, which is also readily available. Thus, we here describe the syntheses and characterizations of several clusters derived by reaction of these molecules with dicobalt octacarbonyl.

Results and Discussion

The reaction of DDT with $Co_2(CO)_8$ proceeds normally in that, upon heating, carbon monoxide is evolved; after the usual purification procedure, a mixture of black and white crystalline products is obtained. However, even after column chromatography and repeated recrystallizations, the black product (which is obtained in only minor yield)

(1) (a) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (b) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (c) Edidin, R. T.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561. (d) D'Agostino, M. F.; Mlekuz, M.; Kolis, J. W.; Sayer, B. G.; Rodger, C. A.; Halet, J.-F.; Saillard, J.-Y.; McGlinchey, M. J. *Organometallics* **1986**, *5*, 2345.

(2) Fieser, L. F.; Fieser, M. *Organic Chemistry*, 3rd ed.; Reinhold: New York, 1956.

0276-7333/90/2309-0020$02.50/0