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Cocondensation of Chromium, Molybdenum, and Tungsten Vapors with Arenes and Phosphorus Ligands

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Cocondensation of chromium vapors with $P(OR)_3$ yields $Cr(P(OR)_3)_6$ in good yield when R = Me. When R = Et, the complex is formed at low temperatures and can be observed at room temperature, but steric interactions between ligands cause the complex to decompose upon attempted isolation. Both complexes can be reacted with H_2 to form the respective $CrH_2(P(OR)_3)_5$ complexes. Simultaneous cocondensation of Cr with $P(OR)_3$ and an arene results in good isolated yields of $Cr(\eta^6\text{-arene})(P(OR)_3)_3$ complexes. Cocondensation of resistively heated Cr or electron beam heated Mo and W with arenes gives the expected $M(\eta^6\text{-arene})_2$ complexes. Cocondensation of Mo in $P(OMe)_3$ gives a low yield of $Mo(P(OMe)_3)_6$, and with W in $P(OMe)_3$, a slurry of W metal in $P(OMe)_3$ is the only product obtained directly. The high radiant energy from the evaporation source coupled with the photolytic instability of $Mo(P(OMe)_3)_6$ and the W analogue leads to decomposition of the desired products. $W(P(OMe)_3)_6$ can be formed by heating the slurry of W in $P(OMe)_3$.

Introduction

The literature on metal vapor synthesis of binary, zerovalent $Cr(\eta^6\text{-arene})_2$ complexes is extensive.[1,2] For reasons of technical difficulty, the vapor chemistry of Mo[2,3] and W[2,4] with arenes is less well developed. The binary, group 6 complexes with fluorophosphines have been prepared photochemically[5] and by vapor synthesis techniques.[6] Choi and Muetterties[7a] have recently presented a concise status of the field of binary, zerovalent transition-metal phosphite complexes. The phosphite complex, $Mo(P(OMe)_3)_6$,[7] has been known for some time,[8] but the chromium[9] and tungsten[7a,10] derivatives as well as the phosphine complex $Mo(PMe_3)_6$[11] have been reported only recently.

Ternary $M(\eta^6\text{-arene})L_3$ are well-known when L is CO or a fluorophosphine.[12] There has also been some effort to extend the ternary systems to other phosphorus ligands,[13] particularly for molybdenum.[14] Especially interesting was the preparation of "$Mo(PMe_2Ph)_4$",[15] which turned out to be $Mo(PMe_2Ph)_3(\eta^6\text{-}C_6H_5PMe_2)$.[16]

We have a longstanding interest in phosphorus ligand complexes and the influence of steric and electronic properties of these ligands.[17] The metal vapor technique would appear well suited to the synthesis of binary zerovalent complexes. We, therefore, decided to extend our studies to the group 6 triad. Initial results have been communicated;[9] the details of the study are reported in this and another paper.[18]

Experimental Section

Vapor syntheses involving chromium were carried out in an apparatus similar to that described by Skell[19] with our own modifications[20] (see Figure 1). The general procedures have been discussed earlier.[20,21] Reactions involving Mo or W were carried out in a Planar VSP-302 vapor synthesis plant using reversed-polarity electron beam heating. Except where noted, the cocondensates were removed from the evaporation apparati under an atmosphere of prepurified argon. All subsequent manipulations were carried out in a Vacuum Atmospheres drybox flushed with dry nitrogen. Solvents and excess ligands were removed on a rotary evaporator in the drybox or on a standard high-vacuum line. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker HFX-90 spectrometer at 36.43 MHz and are reported as positive downfield from external H_3PO_4. ^{13}C NMR spectra recorded on a Bruker WH-90 and proton spectra recorded on Varian HR-220 and XL-100 spectrometers are reported positive downfield from internal Me_4Si. All spectra were recorded in toluene-d_8 unless otherwise indicated. Analyses were carried out at our analytical facilities and were satisfactory.

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(1) (a) Timms, P. L. *Chem. Commun.* **1969**, 1033. (b) Timms, P. L. *J. Chem. Educ.* **1972**, *49*, 782. (c) Skell, P. S.; William-Smith, D. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 3337. (d) Klabunde, K. J.; Efner, H. F. *Inorg. Chem.* **1975**, *14*, 789. (e) Graves, V.; Lagowski, J. J. *Inorg. Chem.* **1976**, *15*, 577. (f) Efner, H. F.; Fox, W. B.; Smardezewski, R. R.; Tevault, O. E. *Inorg. Chim. Acta* **1977**, *24*, L93.

(2) Blackborow, J. R.; Young, D. "Metal Vapor Synthesis in Organometallic Chemistry"; Springer-Verlag: Berlin, Heidelberg, New York, 1979; see pp 120–122 for a list of other Cr arene references.

(3) (a) Benfield, F. W. S.; Green, M. L. H.; Ogden, J. G.; Young, D. *Chem. Commun.* **1973**, 866. (b) Boyd, J. W.; Lavoie, J. M.; Green, D. M. *J. Chem. Phys.* **1974**, *60*, 4088.

(4) (a) Silvon, M. P.; van Dam, E. M.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 1945. (b) Cloke, F. G. N.; Green, M. L. H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1978**, 72.

(5) Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1972**, *11*, 1858.

(6) (a) Timms, P. L. *J. Chem. Soc. A* **1970**, 2526. (b) Sneddon, L. G.; Lagow, P. J. *Chem. Commun.* **1975**, 302. (c) Timms, P. L.; Turney, T. W. *Adv. Organomet. Chem.* **1977**, *15*, 53.

(7) (a) Choi, H. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 153. (b) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056.

(8) Mathiev, R.; Poilblanc, R. *Inorg. Chem.* **1972**, *11*, 1858.

(9) (a) Ittel, S. D.; Tolman, C. A. U.S. Patent 4 155 925, 1979. (b) Van-Catledge, F. A.; Ittel, S. D.; Tolman, C. A.; Jesson, J. P. *J. Chem. Soc., Chem. Commun.* **1980**, 254.

(10) Choi, H. W.; Gavin, R. M.; Muetterties, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1085.

(11) Cloke, F. G. N.; Cox, K. P.; Green, M. L. H.; Bashkin, J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 393.

(12) (a) Nixon, J. F. *J. Fluorine Chem.* **1973**, *3*, 179. (b) Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 120. (c) Timms, P. L. *Angew Chem., Int. Ed. Engl.* **1975**, *14*, 273. (d) Blackborow, J. R.; Grubbs, R.; Miyashita, A.; Scrivanti, A. *J. Organomet. Chem.* **1976**, C49. (e) Nesmeyanov, A. N.; Krivykh, V. V.; Panosyan, G. A.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1979**, *164*, 167.

(13) Kuendil, E. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 991.

(14) (a) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc. A* **1971**, 2929. (b) Green, M. L. H.; Knight, J.; Mitchard, L. C.; Roberts, G. G.; Silverthorn, W. E. *J. Chem. Soc. D* **1971**, 1619. (c) Green, M. L. H.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1973**, 301. (d) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1361. (e) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1139. (f) Davies, M. C.; George, T. A. *J. Organomet. Chem.* **1982**, *224*, C25.

(15) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639.

(16) Mason, R.; Thomas, K. M.; Heath, G. A. *J. Organomet. Chem.* **1975**, *90*, 195.

(17) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) English, A. D.; Ittel, S. D.; Tolman, C. A.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 117. (c) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432.

(18) Van-Catledge, F. A.; Ittel, S. D.; Jesson, J. P. *Organometallics* **1985**, *4*, 18.

(19) Skell, P. S.; Wescott, L. D. *J. Am. Chem. Soc.* **1963**, *85*, 1023.

(20) (a) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 3874. (b) Ittel, S. D.; Tolman, C. A. *Organometallics* **1982**, *1*, 1432.

(21) For a general introduction to the metal vapor synthesis technique, see: (a) *Inorg. Synth.* **1979**, *19*, 59. (b) Klabunde, K. J. "Chemistry of Free Atoms and Particles"; Academic Press: New York, 1980. (c) Blackborow, J. R.; Young, D. "Metal Vapor Synthesis in Organometallic Chemistry"; Springer-Verlag: Berlin 1979.

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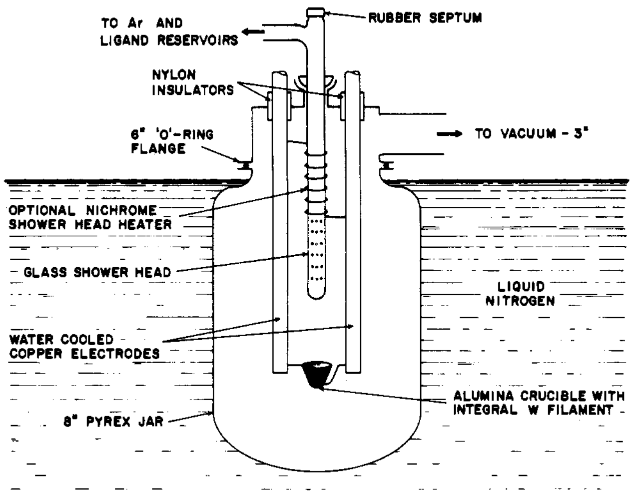

Figure 1. Local design of the metal vapor apparatus.

The arenes and phosphites are commercially available and were used after filtration through neutral-grade alumina and degassing. Solvents were dried by standard techniques.

Preparation of $Cr(P(OMe)_3)_6$. The liquid-nitrogen-cooled flask was coated with 30 mL of pentane. Trimethyl phosphite was then condensed into the flask at about 1 mL min^{-1}. Over a period of 2.5 h, approximately 13 g of chromium metal was evaporated into 175 mL of trimethyl phosphite. After the cocondensation was terminated, an additional 30 mL of pentane was condensed into the reaction flask, and the mixture was allowed to warm to room temperature with magnetic stirring. The mixture was filtered through diatomaceous earth, and then volatiles were removed under vacuum. The tacky, dark solids were extracted with pentane and again filtered through diatomaceous earth and then activated carbon. Filtration through Woelm neutral-grade alumina (activity 1) gave a yellow solution that yielded yellow $Cr(P(OMe)_3)_6$ upon evaporation and drying under high vacuum at $\sim$-20 °C. A typical yield on this scale is 5–15 g with no apparent reason for the variability. The $^{31}P\{^1H\}$ and ^1H NMR spectra were single lines at 196.3 and 3.6 ppm, respectively. Anal. Calcd for $Cr(P(OMe)_3)_6$: C, 27.15; H, 6.84; P, 23.3. Found: C, 27.01; H, 6.79; P, 23.6. Mp: $\sim$100 °C dec.

Preparation and Attempted Isolation of $Cr(P(OEt)_3)_6$. The cocondensation procedure was similar to that for the $P(OMe)_3$ derivative. After filtration through diatomaceous earth and alumina, the clear yellow solution displayed $^{31}P\{^1H\}$ NMR resonances at 137.8 and 191.3 ppm corresponding to free $P(OEt)_3$ and $Cr(P(OEt)_3)_6$, respectively. As the pentane solvent and excess $P(OEt)_3$ were removed under vacuum at room temperature, the solution darkened and Cr metal began to precipitate. After volatiles had been removed, the remaining small quantity of dark tarry residue was extracted with pentane, leaving a fine dark powder. $^{31}P\{^1H\}$ NMR of the pentane solution indicated free phosphite with no $Cr(P(OEt)_3)_6$.

Preparations. $Cr(P(OMe)_3)_5H_2$. A solution of $Cr(P(OMe)_3)_6$ (2.39 g) in toluene (30 mL) was pressurized under H_2 at 20 psig at room temperature in a magnetically stirred glass vessel. After 1 h, the volatiles were removed under vacuum. The residue was taken up in pentane, chromatographed on degassed Woelm neutral-grade alumina, and evaporated to give $Cr(P(OMe)_3)_5H_2$ as an off-white solid. At room temperature, the ^1H NMR spectrum displayed a singlet at 3.64 ppm and a sextet at -7.71 ppm (J_{PH} = 53.3 Hz) for phosphite methyls and hydride, respectively. The room-temperature $^{31}P\{^1H\}$ NMR spectrum consisted of a single line at 201.4 ppm (in toluene-d_8). At low temperatures, broadening is observed until finally, at -120 °C, a non-first-order AB_2C_2 spectrum is obtained (in $CHClF_2$). Isolated yields were approximately 50%, but NMR yields indicated quantitative conversion. Anal. Calcd for $Cr(P(OMe)_3)_5H_2$: C, 26.72; H, 7.03; P, 23.0. Found: C, 26.87; H, 7.00; P, 23.9. Mp: $\sim$130 °C dec.

$Cr(P(OEt)_3)_5H_2$. Chromium and $P(OEt)_3$ were cocondensed as in the previous examples. When the cocondensation was complete, the reactor flask was back-filled with hydrogen to 600 torr at -196 °C. The pressure was maintained at 600 torr as the mixture was allowed to warm to room temperature and stirred for 24 h. Workup was similar to previous examples. The final product was a yellow solid that darkened upon standing at room temperature but was stable indefinitely at -40 °C. The characteristic hydride resonance was a sextet at -7.60 ppm, J_{PH} = 54.6 Hz. At room temperature the $^{31}P\{^1H\}$ NMR spectrum consisted of a single line at 195.8 ppm that split into a complex AB_2C_2 system at -90 °C. Yields were considerably less than observed in the $P(OMe)_3$ system, ranging from 1 to 3 g. Anal. Calcd for $Cr(P(OEt)_3)_5H_2$: C, 40.72; H, 8.77; P, 17.5. Found: C, 40.82; H, 8.82; P, 18.2. Mp: onset of thermal decomposition too rapid for any meaningful determination.

Hydrogenation of 1-Hexene. Either $Cr(P(OMe)_3)_6$ (0.080 g) or $Cr(P(OMe)_3)_5H_2$ (0.067 g) was dissolved in 10 mL of toluene, and 1.25 mL of hexene was added. The mixture was then pressured to 25 psig with H_2. The mixture was then stirred at 25 °C for 1–2 h. Gas–liquid chromatography of the liquid product showed that between 3 and 4 equiv of hexane had been formed per equivalent of chromium. No methylcyclohexane was observed, indicating that toluene was not hydrogenated.

Preparations. $W(\eta^6\text{-Tol})_2$ (Tol = Toluene). A tungsten rod was carefully outgassed by slowly heating with the electron beam. At the first sign of metal evaporation, power was reduced and condensation of toluene on the walls of the rotating flask was initiated. After 30 mL of toluene had been condensed into the reactor, electron beam power was once again increased (to 1500–1800 W), and tungsten cocondensation was begun. When the vapor pressure inside the flask was too high, the electron beam high voltage arced to ground with UV output and interruption of power. This occurs when the toluene input is too high or too much power is applied to the molten tungsten. The latter problem is especially critical in later stages of the run when there is an appreciable buildup of material on the flask walls. (Thermal conduction decreases, and absorption of radiant energy increases.) When the run was complete or electron beam power could no longer be maintained, the vacuum was shut off. After melting, the contents of the reactor were transferred to a Schlenk tube. Workup consisted of filtration, removal of volatiles, and a final recrystallization of the green residue from pentane to give a green powder; yield typically 1–2 g. ^1H NMR: η^6-phenyl, δ 5.05 (br); Me, δ 2.10 (s). Bis(toluene)molybdenum was prepared similarly.

$Mo(P(OMe)_3)_6$. The reaction was carried out in a manner similar to that described for $W(Tol)_2$. Approximately 3 g of Mo were cocondensed with $P(OMe)_3$ over a period of 2.5 h. After the cocondensation was complete, a layer of pentane was condensed into the flask, and the entire mixture was allowed to warm to room temperature. Filtration and removal of volatiles left an off-white tacky residue. Recrystallization from pentane gave colorless crystals; yield 0.3 g. ^1H NMR: δ 3.7 (m). $^{31}P\{^1H\}$ NMR δ 172.5 (s with two barely resolved satellite sextets; $J_{P-^{95}Mo}$ = 253 Hz, 15.7% natural abundance; $J_{P-^{97}Mo}$ = 256 Hz, 9.5% natural abundance).[22]

Attempted Preparation of $W(P(OMe)_3)_6$. A procedure similar to that used for $W(Tol)_2$ was used in an attempt to prepare $W(P(OMe)_3)_6$. After filtration of the cocondensate, removal of volatiles left a film of oily material on the walls of the vacuum flask. $^{31}P\{^1H\}$ NMR of a concentrated pentane extract revealed no resonances assignable to a tungsten complex.

Preparation of $W(P(OMe)_3)_6$. The cocondensation procedure was repeated, but no pentane was included. The $P(OMe)_3$ suspension of W was transferred to a Schlenk flask and refluxed under N_2 for 1 h. Removal of volatiles under vacuum gave a black residue that was extracted with pentane. Evaporation of the extract and several further recrystallizations from pentane gave colorless crystals of $W(P(OMe)_3)_6$; yield 1.2 g. ^1H NMR: δ 3.7 (m). $^{31}P\{^1H\}$: δ 143.3 (s with satellite doublet; J = 449 Hz for ^{183}W, 14.4% natural abundance).

Decomposition of $W(P(OMe)_3)_6$ in a Cryogenic Matrix. A solution of $W(P(OMe)_3)_6$ (0.1 g) in $P(OMe)_3$ (2 mL) in a quartz tube was quenched in liquid nitrogen to give a glass. The sample was then exposed to a 300-W incandescent bulb for 20 min. The sample was warmed, and volatiles were removed under vacuum. The residue was extracted with pentane, and the resulting solution was studied by ^{31}P NMR after filtration. The only resonances were those of residual $P(OMe)_3$ and $MeP(O)(OMe)_2$; no $W(P(OMe)_3)_6$ was observed. A similar sample, which was kept in the dark, gave a strong ^{31}P signal for $W(P(OMe)_3)_6$.

Synthesis of $Cr(\eta^6\text{-Tol})(P(OMe)_3)_3$. The walls of the reactor were coated with 60 mL of diethyl ether. Chromium was then evaporated at $\sim$3 g h^{-1} into a mixture of $P(OMe)_3$ and toluene that were both condensed into the reactor at about 1 mL min^{-1}. When the cocondensation

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(22) These ^{95}Mo–^{31}P coupling constants are similar to those observed for other molybdenum phosphite or PF_3 complexes discussed in ref 7a or: (a) Baily, J. T. Clark, R. J.; Levy, G. C. *Inorg. Chem.* **1982**, *21*, 2085. (b) Alyea, E. C.; Lenkinski, R. E.; Somogyuari, A. *Polyhedron* **1982**, *1*, 130. (c) Febuay, J.; Grec, E.; Riess, J. G. *Inorg. Chem.* **1981**, *20*, 4285.

was complete (~2.5 h), an additional 60 mL of diethyl ether was condensed into the reactor and then the entire mixture was allowed to warm to room temperature with stirring. The mixture was filtered through diatomaceous earth, and volatiles were removed under vacuum. A pentane solution was filtered through neutral-grade alumina, and volatiles were once again removed. Recrystallization from pentane gave yellow orange solids; yield 10.0 g. ^{1}H NMR: toluene-H, δ 4.7–4.2 (m); toluene-Me, δ 2.24 (s); $P(OMe)_3$, δ 3.48 (m). $^{31}P\{^1H\}$ NMR: δ 214.7 (s). Anal. Calcd for $Cr(P(OMe)_3)_3(C_6H_5Me)$: C, 37.22; H, 6.40; P, 18.0. Found: C, 37.12; H, 6.45; P, 18.4.

Preparation of $Cr(\eta^6\text{-Mesit})(P(OMe)_3)_3$ (Mesit = Mesitylene). This compound was prepared in a manner similar to that described for the related toluene complex. Evaporation was carried out for 3 h; yield 12.7 g. ^{1}H NMR: Mesit-H, δ 4.18 (quart, J_{PH} = 2 Hz); Mesit-Me, δ 2.20 (s); $P(OMe)_3$, δ 3.54, (m). $^{31}P\{^1H\}$ NMR: δ 213.6 (s). Anal. Calcd for $Cr(P(OMe)_3)_3(C_6H_3Me_3)$: C, 39.71; H, 7.22; P, 17.1. Found: C, 39.82; H, 7.29; P, 18.0.

Results and Discussion

Cocondensation of chromium vapors with trimethyl phosphite onto a liquid-nitrogen-cooled surface results in a mixture of bulk chromium metal, free trimethyl phosphite, and $Cr(P(OMe)_3)_6$. The desired complex can be isolated in good yield by filtration, vacuum removal of volatiles, and extraction of the resultant residue with pentane. The complex is extremely soluble in pentane but can be obtained as an off-white crystalline solid by removal of the pentane at low temperature under high vacuum.

When the procedure is repeated with triethyl phosphite, the cocondensation mixture is almost identical. After filtration, the crude $Cr(P(OEt)_3)_6$ can be observed by NMR in the excess phosphite. As phosphite is removed at room temperature under vacuum, however, the concentration of complex in the remaining ligand does not appear to increase as fast as one might expect, and additional chromium metal is precipitated. By the time the mixture has been pumped to tacky solids, it is very dark and little complex remains. $Cr(P(OEt)_3)_6$ is apparently unstable with respect to free ligand and bulk metal; all of the phosphite essentially has been pumped off the metal.

As part of a series of NMR experiments, we discovered that $Cr(P(OMe)_3)_6$ reacts rapidly in the dark[7] with hydrogen to form the seven-coordinate Cr(II) complex, $Cr(P(OMe)_3)_5H_2$. (The NMR spectroscopic characterization of this complex is reported elsewhere.[9,18]) With this observation in hand, the preparation of $Cr(P(OR)_3)_5H_2$ complexes became relatively easy: the cocondensates of chromium with $P(OMe)_3$ and $P(OEt)_3$ were allowed to warm to room temperature under an atmosphere of H_2 rather than Ar. The corresponding dihydrides were readily isolated from the resultant mixtures.

These observations indicate that alkyl phosphite complexes of chromium are very sterically crowded, as one might predict. Changing from $P(OMe)_3$ to $P(OEt)_3$ increases the cone angle of each of the six coordinated phosphorus ligands by just 2° ($P(OMe)_3$, $\theta = 107°$; $P(OEt)_3$, $\theta = 109°$),[17a] yet this is enough to tip the balance from isolable to nonisolable. When one phosphorus ligand is replaced by two hydrides, the steric strain is relieved and both the $P(OMe)_3$ and $P(OEt)_3$ derivatives can be isolated. (While it might appear that two hydrides ($\theta = 75°$)[17a] would require more area on the surface of the transition-metal center, they are well inside the critical outer sphere of phosphite methyl groups where the important van der Waals interactions are occurring.)

As a test of our ability to carry out metal vapor syntheses with Mo and W, we condensed the respective metals with toluene. While the Planar vapor synthesis plant, VSP-302, is capable of vaporizing tungsten at rates up to 5 g h^{-1}, we found that much lower rates gave the best yields of the arene complexes. Both $Mo(\eta^6\text{-Tol})_2$ and $W(\eta^6\text{-Tol})$ were isolated in good yield in experiments very similar to those reported by Green.[4]

When we proceeded to trimethyl phosphite, the results were disappointing. We were able to isolate $Mo(P(OMe)_3)_6$ in only a poor yield, and we observed no $W(P(OMe)_3)_6$ in the crude mixture from the tungsten phosphite cocondensation. At first, these results were confusing in light of the prior syntheses of these species, but Muetterties' publication[10] of the properties of $W(P(OMe)_3)_6$ presented a reasonable answer. $Mo(P(OMe)_3)_6$ and especially $W(P(OMe)_3)_6$ are photosensitive, dissociating ligands upon photolysis. Exposure to room light will decompose the tungsten complex. In the metal vapor syntheses technique, the product matrix is necessarily exposed to the light emitted from the evaporating metal surface, and when the metal is tungsten, the radiation is so intense that one must use welders' glasses to look at the metal surface. Figure 2 presents the relative, emissivity corrected, radiation curves for blackbody radiation at the vaporization temperatures employed for Cr, Mo, and W. Molten metal surfaces are far from ideal blackbodies, having relatively low emissitivities, but nonetheless, appreciable quantities of relatively high-energy radiation impinge upon the cocondensate surface, especially for tungsten. Thus, with a 1500-W light source in the middle of the flask, it is not at all surprising that any $W(P(OMe)_3)_6$, which might be formed, is photolyzed as quickly as it is produced.[23] This concept is simply tested by freezing $W(P(OMe)_3)_6$ in a $P(OMe)_3$ matrix. We find it is largely decomposed when exposed to the light emitted by solid tungsten just below its melting point.

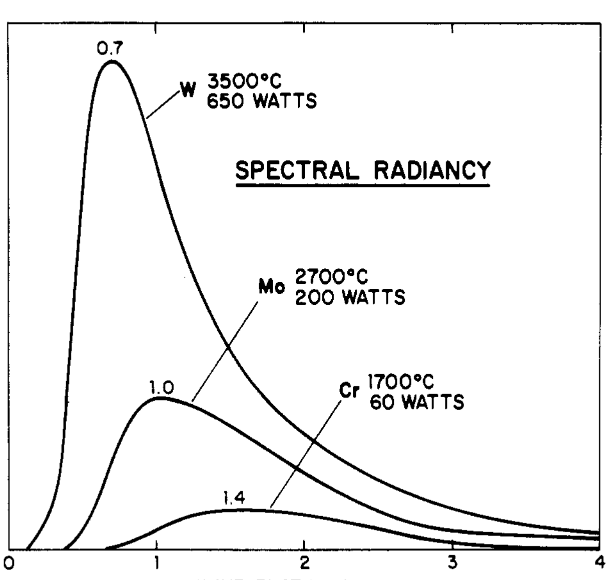

Figure 2. Relative spectral radiancies for 1-cm^2 surfaces of molten Cr, Mo, and W at temperatures appropriate for vapor synthesis. For Cr in an alumina crucible, there is also appreciable radiation from the crucible walls. For Mo and W in an electron beam heater, the majority of the power applied is carried away from the bottom of the sample by cooling water circulating through the copper hearth.

We could conceive of no reasonable method to circumvent the photochemistry going on in the reactor. Still wanting to prepare $W(P(OMe)_3)_6$ and taking a lead from Muetterties' published syntheses,[10] we reasoned that we had prepared a slurry of very active tungsten metal in $P(OMe)_3$. When our vapor prepared slurry is refluxed, a small fraction of the bulk metal is converted to the desired $W(P(OMe)_3)_6$. Thus, a circuitous vapor synthesis of $W(P(OMe)_3)_6$ is possible.

The cocondensation of chromium atoms with trimethylphosphine gave a brown matrix from which we were able to isolate no products. In light of the problems with alkyl phosphites it is no surprise that $Cr(PMe_3)_6$ is not formed. We had hoped that

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(23) Klabunde has carried out a very elegant study of photolysis and thermolysis reactions as they affect the cocondensation technique and found thermolysis to be dominant: Klabunde, K. J.; Groshens, T.; Efner, H. F.; Kramer, M. *J. Organomet. Chem.* **1978**, *157*, 91. Considering our reactor geometry, limited pyrolytic surfaces, and the known photoinstability of the $M(P(OMe)_3)_6$ complexes, we feel that thermolysis reactions do not make a significant contribution to the observed decomposition reactions.

it might be possible to isolate compounds similar to those from the iron trimethylphosphine cocondensation—$Fe(PMe_3)_3H(CH_2PMe_2)$—in which an initial coordinatively unsaturated zerovalent product fulfills the noble gas configuration by oxidative addition of C–H bonds. A recent report from Green's laboratory indicates that $Mo(PMe_3)_6$ can be prepared and that, in fact, it is in a reversible equilibrium with $Mo(PMe_3)_4H(CH_2PMe_2)$ and $Mo(PMe_3)_2H_2(CH_2PMe_2)_2$.

Having prepared the binary phosphite and arene complexes, we decided to attempt the ternary synthesis of $Cr(arene)(P(OMe)_3)_3$ complexes. We expected this synthesis to require a separation of the desired product from the binary products, $Cr(arene)_2$ and $Cr(P(OMe)_3)_6$. In fact, the ternary complex is formed in high yield and relatively free of either binary product. A simple recrystallization is sufficient to give analytically pure material. It is not surprising that the arene tris(phosphite) complex would be favored over the hexakis(phosphite) complex simply on the grounds of steric constraints. One π arene would cause less steric interaction than three phosphites. We do find it remarkable that the yield of the bis(arene) is low. The well-known preparative chemistry of these compounds is some indication of their stability, yet the mixed complex must be even more stable.

Registry No. $Cr(P(OMe)_3)_6$, 70948-62-8; $Cr(P(OEt)_3)_6$, 70948-60-6; $Cr(P(OMe)_3)_5H_2$, 70948-61-7; $Cr(P(OEt)_3)_5H_2$, 70948-59-3; $W(\eta^6\text{-tol})_2$, 52346-44-8; $Mo(\eta^6\text{-tol})_2$, 12131-22-5; $Mo(P(OMe)_3)_6$, 37478-27-6; $W(P(OMe)_3)_6$, 73411-63-9; $Cr(\eta^6\text{-tol})(P(OMe)_3)_3$, 93646-60-7; $Cr(\eta^6\text{-Mesit})(P(OMe)_3)_3$, 93646-61-8; $P(OEt)_3$, 122-52-1; $P(OMe)_3$, 121-45-9; Cr, 7440-47-3; W, 7440-33-7; Mo, 7439-98-7; $P(O)(OMe)_2$, 16038-03-2; toluene, 108-88-3; 1-hexene, 592-41-6; hexane, 110-54-3; mesitylene, 108-67-8.

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Surface Coordination Chemistry of Platinum Studied by Thin-Layer Electrodes.[1] Adsorption, Orientation, and Mode of Binding of Aromatic and Quinonoid Compounds

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Extensive studies on the interaction of 54 aromatic and quinonoid compounds with smooth Pt thin-layer electrodes have yielded data that serve to establish the surface coordination chemistry of polycrystalline Pt with these compounds in aqueous solutions. Adsorption of the subject compounds occurred spontaneously and irreversibly at specific orientations which depended on their characteristic molecular structures and concentrations, C^0. These orientations have been represented in terms of modes of coordination derived from model compounds; supportive electrochemical and infrared spectroscopic data are presented. For simple *o*- and *p*-diphenols or quinones, adsorption at $C^0 \leq 0.1$ mM produced flat-oriented (π-bonded) quinone intermediates; adsorption at $C^0 \geq 1$ mM resulted in edge-oriented (di-σ-bonded) diphenolic species. When the Pt surface was purposely pretreated with π-bonded intermediates, severe reorientation retardation was observed, indicating that adsorption from concentrated solutions does not involve coordination in the flat orientation as an intermediate step. Substituents on or heteroatoms in the aromatic/quinonoid ring altered its surface coordination properties to varying degrees; analysis of the adsorption/orientation data enabled the formulation of a strength-of-chemisorption series for the various organic functional groups investigated. The effect of temperature on surface properties has been described in terms of perturbations to the preferred modes of attachment. Fluxional motion of chemisorbed 3,6-dihydroxypyridazine was indicated near 65 °C, similar to that of pyridazine itself in Pt coordination compounds.

Introduction

The study of heterogeneous catalytic reactions has always been concerned with the nature of intermediates present on the catalyst surface. One approach involves characterization of surface species prior to and after occurrence of a catalytic reaction. Elegant surface analytical techniques have proliferated[3] for this purpose, although many are limited to ultrahigh vacuum (UHV). Chemical representations of surface compounds are vital and have generally been derived from concepts in coordination and organometallic chemistry.[4]

We have recently studied the interaction of aromatic and quinonoid compounds with platinum[2] thin-layer electrodes[5] in an effort to determine adsorbed reaction intermediates and their influences on bulk electrocatalytic processes. An offshoot of this work has been the accumulation of data that serve to establish the surface coordination chemistry of platinum metal with the subject compounds in aqueous solutions. Qualitative description of such chemistry, as outlined in Table I, is the purpose of these articles. The adsorption and orientation of aromatic/quinonoid compounds are described in this paper, along with the representation of adsorbed molecule orientation in terms of modes of coordination derived from model, well-characterized molecular

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(2) (a) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 2735. (b) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 2742. (c) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3937. (d) Soriaga, M. P.; Wilson, P. H.; Hubbard, A. T.; Benton, C. S. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *142*, 317. (e) Chia, V. K. F.; Soriaga, M. P.; Hubbard, A. T.; Anderson, S. E. *J. Phys. Chem.* **1983**, *87*, 232. (f) Soriaga, M. P.; White, J. H.; Hubbard, A. T. *J. Phys. Chem.* **1983**, *87*, 3048. (g) Stickney, J. L.; Soriaga, M. P.; Hubbard, A. T.; Anderson, S. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *125*, 73. (h) Soriaga, M. P.; Stickney, J. L.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *144*, 207. (i) Soriaga, M. P.; Stickney, J. L.; Hubbard, A. T. *J. Mol. Catal.* **1983**, *21*, 211. (j) Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *159*, 101. (k) Soriaga, M. P.; Hubbard, A. T. *J. Phys. Chem.* **1984**, *88*, 1758. (l) Soriaga, M. P.; Hubbard, A. T. *J. Phys. Chem.* **1984**, *88*, 1089. (m) Soriaga, M. P.; Chia, V. K. F.; White, J. H.; Song, D.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *162*, 143. (n) Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *167*, 79. (o) Chia, V. K. F.; Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *167*, 97. (p) Soriaga, M. P.; White, J. H.; Song, D.; Hubbard, A. T. *J. Phys. Chem.* **1984**, *88*, 2284. (q) Soriaga, M. P.; White, J. H.; Song, D.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *171*, 359.

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