Stabilization of R–P(H)A Species (A = OH, OR, S–, NH_2, NHR, NR_2, Cl, Br, I) by Complexation with Chromium and Tungsten Pentacarbonyls

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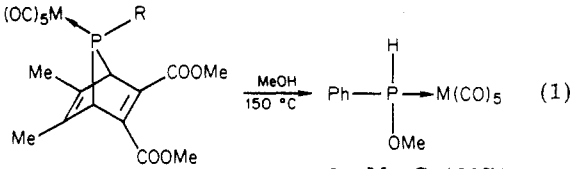
The 7-phosphanorbornadiene complexes of chromium and tungsten pentacarbonyls react between 120 and 150 °C with AH (AH = H_2O, MeOH, $PhNH_2$, Et_2NH) to give the corresponding $[RP(H)A]M(CO)_5$ secondary phosphine complexes (R = Ph, Me) through cleavage of the phosphorus bridge of the phosphanorbornadiene skeleton. The phosphorus–hydrogen bond of these compounds is very resistant toward oxidation. In one case, it has been successfully metalated by *t*-BuOK in THF and, then, either alkylated by methyl iodide or condensed with benzophenone. The phosphorus–nitrogen bond of $[PhP(H)(NHPh)]W(CO)_5$ is easily cleaved at room temperature by hydrogen halides to give the first known stable secondary halophosphine complexes $[PhP(H)X]W(CO)_5$ (X = Cl, Br, I). The chloro compound reacts with ammonia and NaSH at room temperature to give, respectively, $[PhP(H)NH_2]W(CO)_5$ and $S[PhPH{\rightarrow}W(CO)_5]_2$. In the presence of aluminum trichloride, the dismutation of the chloro compound yields equal amounts of $[PhPH_2]W(CO)_5$ and $[PhPCl_2]W(CO)_5$. All these compounds are stable and have been completely characterized by ^1H NMR, ^{31}P NMR, IR, and mass spectrometry and elemental analyses.

Phosphines such as R–P(H)A, where R stands for a hydrocarbon group and A for an electronegative group, are normally unstable because they tend to lose AH and to give the corresponding cyclopolyphosphine, $(RP)_n$. As far as we know, the only significant exception has been recently described in the literature for R = CF_3 and A = Cl, Br, and I;[1] the corresponding secondary halophosphines are just stable enough toward dismutation and redistribution to allow their characterization. On the other hand, we have shown in a previous communication[2] that the more conventional *O*-methyl phenylphosphinite was stabilized by complexation with tungsten pentacarbonyl. In a similar vein, Huttner previously reported[3] that it was possible to stabilize secondary phosphines with R = Ph and A = OR, NHR, and NR_2 by complexation with $CpMn(CO)_2$. The corresponding chlorophosphine complex (R = Ph, A = Cl) was not obtained in the pure state and decomposed above −30 °C.

On the basis of these results, we decided to investigate in depth what kind of electronegative A groups could coexist with hydrogen in the coordination sphere of phosphorus when the corresponding secondary phosphines were complexed with $Cr(CO)_5$ and $W(CO)_5$.

Results and Discussion

Reaction of 7-Phosphanorbornadiene Complexes with Water, Alcohols, and Amines. Throughout this work our starting products were the 7-phosphanorbornadiene complexes **1a–c** that can be readily prepared by Diels–Alder cycloaddition of the corresponding phosphole P complexes with dimethyl acetylenedicarboxylate.[4] In our preliminary communication,[2] we described the reaction of **1b** with methanol at 150 °C which gave complex **2b** in 87% yield (eq 1). The same reaction was successful with the chromium complex **1a** and gave **2a** in reasonable yield. We went one step further when we discovered that

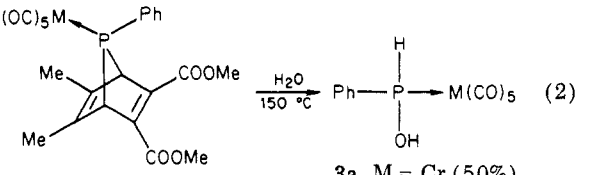


(1)

1a, M = Cr, R = Ph
b, M = W, R = Ph
c, M = W, R = Me

2a, M = Cr (62%)
b, M = W (87%)

it was also possible to add water to the phosphinidene unit by using the same procedure (eq 2). Similarly, complexes

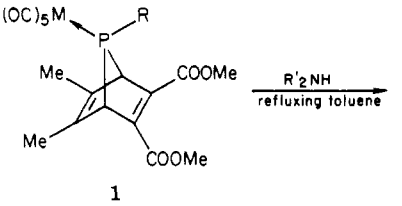


(2)

1

3a, M = Cr (50%)
b, M = W (90%)

1 reacted conveniently with primary and secondary amines to give the expected secondary aminophosphine complexes **4** and **5** (eq 3). We can rationalize these reactions in terms



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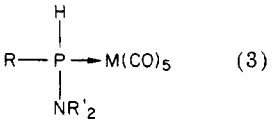

(3)

4a, R'_2N = PhNH, R = Ph, M = Cr (45%)
b, R'_2N = PhNH, R = Ph, M = W (76%)
c, R'_2N = PhNH, R = Me, M = W (14%)
5, R'_2N = Et_2N, R = Ph, M = W (61%)

(1) R. C. Dobbie, P. D. Gosling, and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, 2368 (1975).
(2) A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Am. Chem. Soc.*, **104**, 4484 (1982).
(3) G. Huttner and H. D. Müller, *Angew. Chem., Int. Ed. Engl.* **14**, 571 (1975).
(4) A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Chem. Soc., Chem. Commun.*, 667 (1982).

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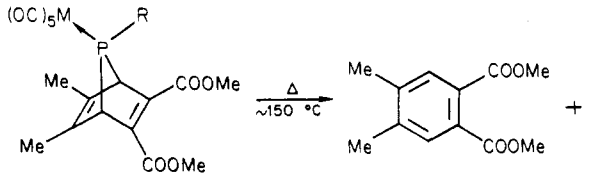
of two mechanisms. In the first, the phosphinidene bridge of complexes 1 is first thermally cleaved in a retro Diels–Alder reaction and, then, the terminal phosphinidene complexes thus obtained react with AH (eq 4). This



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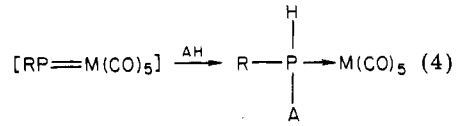
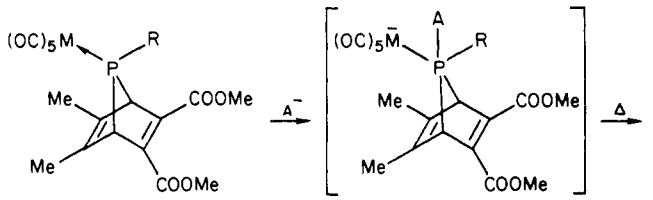


(4)

mechanism is certainly operative when the reactions of 1 are carried out at a sufficiently high temperature and when the phosphinidene unit cycloadds to the conjugated dienes or acetylenes as described in our communication.[2] However, in the case described here, an alternative mechanism is possible which includes preliminary nucleophilic attack of A^- at the phosphorus atom of the phosphanorbornadiene structure (eq 5). The formation of intermediates such as



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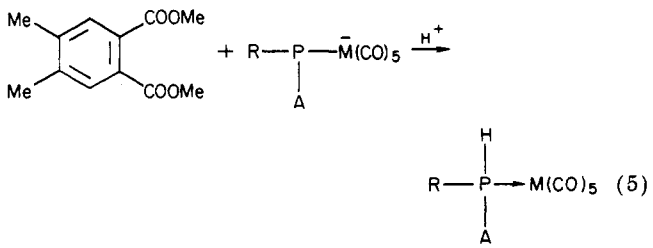
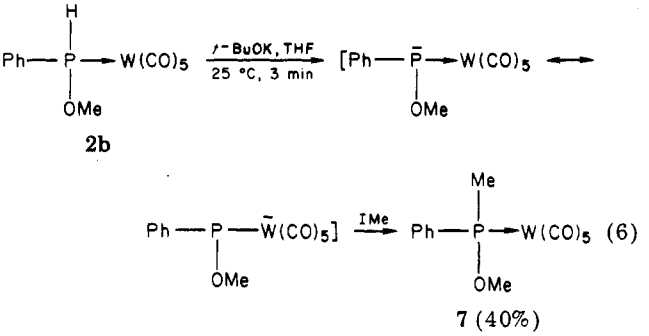


(5)

6 is favored by the high cyclic strain of the phosphanorbornadiene skeleton (intracyclic CPC angle ca. 79°, see ref 4). Furthermore, cyclic phosphoranes of the same type are known[5] to undergo very easily a retro Diels–Alder reaction. Thus, this mechanism is more likely for low-temperature reactions and for nucleophilic reagents, and we favor it, especially in the case of primary and secondary amines.

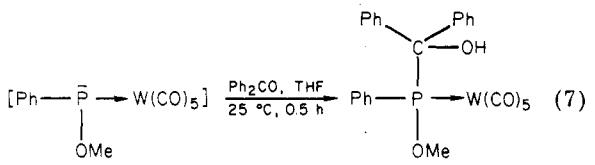
Some Chemistry with Secondary Amino- and Alkoxyphosphine complexes. The availability of stable compounds such as **2–5** gave us the opportunity of checking if the properties of the P–H and P–A bonds were drastically modified by the complexation of phosphorus and by their simultaneous occurrence in the same coordination sphere. The resistance of the P–H bond toward oxidation is noteworthy. All these complexes are easily handled in air and chromatographed without any decomposition. In one significant experiment, we treated **4b** with iodine in benzene at 75 °C. Instead of destroying the P–H bond, we observed the replacement of the amino group by iodine; the corresponding secondary iodophosphine complex **11** was thus obtained in 23% yield (see later). The metalation of the P–H bond can be effected,[6] but the resulting P anion is not very stable and its reactions must be carried out immediately after its generation. Nevertheless, is is possible to alkylate phosphorus conveniently by this technique (eq 6). The same P anion also reacts



2b **7** (40%)

(6)

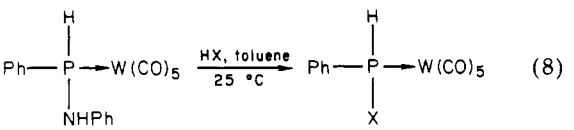
with benzophenone to give the expected alcohol **8** in modest yield (eq 7). The reactivity of the P–A bond[7]



8 (31%)

(7)

appears to decrease (compared to that in uncomplexed P–A compounds), probably for steric reasons, but is less changed than that of the P–H bond. It has already been described in the literature[7] that it is possible to effect reactions of a P–N bond within a $P\rightarrow Mo(CO)_5$ complex with HX to form a phosphorus–halogen bond without destroying the basic structure of the complex. Similarly, we have found that **4b** reacts cleanly with anhydrous hydrogen halides to provide the first known stable complexes of secondary halophosphines (eq 8). Since free secondary



4b

9, X = Cl (74%)
10, X = Br (89%)
11, X = I (81%)

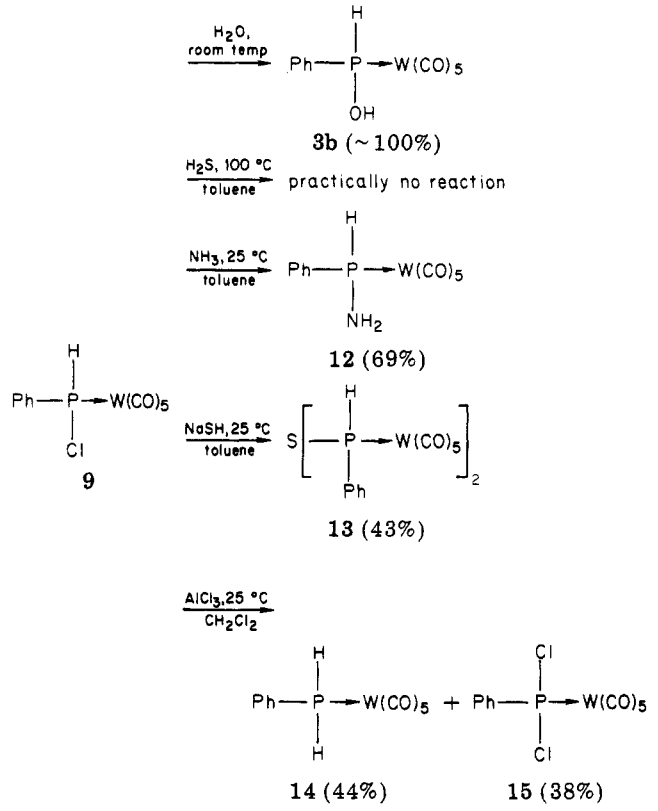
(8)

halophosphines are almost unknown, we decided to carry out a preliminary investigation of the chemical properties of **9**. This complex is thermally stable: it melts at 55 °C and shows no decomposition at 100 °C in toluene for 4 h. It is not oxidizable and reacts slowly with water to give **3b** quantitatively as checked by ^{31}P NMR. Thus, it can be handled in air for a short time without any problem. The low reactivity of **9** is also illustrated by the absence of reaction with hydrogen sulfide at 100 °C in toluene. In

(5) L. D. Quin and K. A. Mesch, *J. Chem. Soc., Chem. Commun.*, 959 (1980).

(6) The metalation of P–H bonds in the coordination sphere of metal carbonyl complexes has already been described by many authors; see, for example: M. Green, A. Taunton-Rigby, and F. G. A. Stone, *J. Chem. Soc. A*, 1875 (1969); P. M. Treichel, W. M. Douglas, and W. K. Dean, *Inorg. Chem.*, **11**, 1615 (1972); *J. Organomet. Chem.*, **42**, 145 (1972); G. Huttner and H. D. Müller, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **30B**, 235 (1975); O. Stelzer and E. Unger, *Chem. Ber.*, **108**, 2232 (1975); O. Stelzer, E. Unger, and V. Wray, *ibid.*, **110**, 3430 (1977); G. Johannsen and O. Stelzer, *ibid.*, **110**, 3438 (1977); P. M. Treichel and W. K. Wong, *J. Organomet. Chem.*, **157**, C5 (1978); *Inorg. Chim. Acta*, **33**, 171 (1979).

(7) For a review on the reactions of the P–A bonds in the coordination spheres of metals, see: C. S. Kraihanzel, *J. Organomet. Chem.*, **73**, 137 (1974). For some more recent references, see: G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem.*, **146**, 23 (1978); **187**, 51 (1980); H. Malisch, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **37B**, 61 (1982).



contrast, the much more nucleophilic ammonia reacts rapidly with **9** at room temperature to give the secondary aminophosphine complex **12** in fair yield. The sulfido derivative **13** is only obtained by replacing H_2S by the more nucleophilic sodium hydrogen sulfide. We have also noted that aluminum trichloride catalyzes the dismutation of **9** into **14** and **15** at room temperature in dichloromethane. The dichloro compound **15** is still more resistant toward hydrolysis than **9** and can be purified by chromatography on silica gel. The bromo- and iodophosphines, **10** and **11**, behave apparently like **9**, but the iodo compound appears to be less thermally stable.

Experimental Section

NMR spectra were recorded on a Bruker WP 80 instrument at 80 and 32.44 MHz, respectively. Chemical shifts are reported in part per million from internal Me_4Si for ^1H and from external H_3PO_4 for ^{31}P: δ positive for downfield shifts in both cases. Mass spectra were recorded on a Nermag R 10-10 spectrometer at 70 eV by Mr Charré (SNPE). All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh Merck) under argon. Spectroscopic data for most products are given in Table I.

[5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonylchromium (1a). (1-Phenyl-3,4-dimethylphosphole)pentacarbonylchromium (4 g, 10.5 mmol) and dimethyl acetylenedicarboxylate (3.8 mL, 31.5 mmol) were heated at 85 °C in toluene for 24 h. After evaporation, the residue was chromatographed with toluene (R_f ~0.5): yield, 2.6 g (47%) of yellow solid; mp 150 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.06 (d, ^4J(H–P) = 1.4 Hz, 6 H, Me), 3.67 (s, 6 H, MeO) 3.98 (d, ^2J(H–P) = 2.5 Hz, 2 H, CH–P), 7.32 (m, 5 H, Ph); ^{31}P NMR (toluene) δ 262.4; ^{13}C NMR (C_6D_6) δ 15.46 (d, ^3J(C–P) = 2.4 Hz, Me–C), 51.68 (s, MeO), 58.89 (d, ^1J(C–P) = 18.3 Hz, CH–P), 126.8–130.7 (Ph), 138.4 (d, J(C–P) = 17.1 Hz, MeC=CMe?), 146.9 (d, ^2J(C–P) = 4.9 Hz, OOCC=CCOO), 164.6 (s, COO), 216.2 (d, ^2J(C–P) = 13.4 Hz, cis CO) (trans CO not detected); IR (decalin) ν(CO) 2062 (m), 1985 (vw), 1955 (sh), 1949 (s), 1941 (s) cm^{-1}; mass spectrum (180 °C), m/e (relative intensity) 522 (M, 0.8), 494 (M – CO, 0.4), 382 (M – 5CO, 7.5), 222 (M – PhPCr(CO)$_5$, 25), 191 (222 – OMe, 100). Anal. Calcd for $C_{23}H_{19}CrO_9P$: C, 52.88; H, 3.67; P, 5.93. Found: C, 52.59; H, 3.55; P, 5.88.

[5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (1b). (1-Phenyl-3,4-dimethylphosphole)pentacarbonyltungsten (4 g, 7.8 mmol) and dimethyl acetylenedicarboxylate (2.8 mL, 23.4 mmol) were heated at 90 °C in toluene (50 mL) for 24 h. After evaporation, the residue was chromatographed with toluene. The starting complex was eluted first (R_f ~0.8), and then **1b** was recovered (R_f ~0.5): yield, 2.7 g (52%) of yellow solid; mp 161 °C (hexane); ^1H NMR ($CDCl_3$) δ 2.05 (d, ^4J(H–P) = 1.5 Hz, 6 H, Me), 3.67 (s, 6 H, MeO), 3.98 (d, ^2J(H–P) = 1.9 Hz, 2 H, CH–P), 7.32 (m, 5 H, Ph); ^{31}P NMR (toluene) δ 208 (^1J(^{183}W–^{31}P) = 236.8 Hz; IR (decalin) ν(CO) 2072 (m), 1985 (vw), 1952 (sh), 1948 (vs), 1942 (sh) cm^{-1}; mass spectrum, see ref 4.

[5,6,7-Trimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene]pentacarbonyltungsten (1c). (1,3,4-Trimethylphosphole)pentacarbonyltungsten (2 g, 4.4 mmol) and dimethyl acetylenedicarboxylate (1.6 mL, 13.2 mmol) were heated at 90 °C in toluene (50 mL) for 15 h. After evaporation, the residue was chromatographed, first with toluene in order to remove the starting complex and then with toluene–ethyl acetate (95:5) to recover **1c**: yield, 2.1 g (80%) of yellow solid; mp 94 °C; ^1H NMR ($CDCl_3$) δ 1.97 (d, ^4J(H–P) = 1.5 Hz, 6 H, Me–C), 1.99 (d, ^2J(H–P) = 3.9 Hz, 3 H, Me–P), 3.56 (d, ^2J(H–P) = 2.7 Hz, 2 H, CH–P), 3.83 (s, 6 H, MeO); ^{31}P NMR (toluene) δ 199.6 (^1J (^{183}W–^{31}P) = 236.8 Hz); IR (decalin) ν(CO) 2070 (m), 1950 (s), 1944 (vs) cm^{-1}.

(*O*-Methyl phenylphosphinite)pentacarbonylchromium (2a). Complex **1a** (1.5 g, 2.9 mmol) was heated at 150 °C for 14 h in a sealed tube with methanol (10 mL) and toluene (10 mL). After evaporation, the residue was chromatographed with hexane–toluene (90:10): R_f ~0.5; yield, 0.6g (62%) of colorless solid; mp 64 °C. Anal. Calcd for $C_{12}H_9CrO_6P$: C, 43.39; H, 2.73; P. 9.32. Found: C, 43.27; H, 2.75; P, 9.05.

(*O*-Methyl phenylphosphinite)pentacarbonyltungsten (2b). Complex **1b** (1 g, 1.5 mmol) was heated at 150 °C for 16 h in a sealed tube with methanol (5 mL) and toluene (10 mL). After evaporation, the residue was chromatographed with hexane–toluene (90:10): R_f ~0.5; yield, 0.6 g (87%) of colorless solid; mp 80 °C; mass spectrum, see ref 2. Anal. Calcd for $C_{12}H_9O_6PW$: C, 31.06; H, 1.95; P, 6.67. Found: C, 31.36; H, 1.95; P, 6.70.

(Phenylphosphinous acid)pentacarbonylchromium (3a). Complex **1a** (1.5 g, 2.9 mmol) was heated at 140 °C for 5 h in a sealed tube with distilled water (0.5 mL) in toluene–THF (75:25). After evaporation, the residue was chromatographed with toluene: yield, 0.44 g (50%) of colorless oil; mass spectrum, m/e (relative intensity) 318 (M, 26), 290 (M – CO, 4), 262 (M – 2CO, 19), 234 (M – 3CO, 11), 206 (M – 4CO, 26), 178 (M – 5CO, 100), 160 (CrPPh, 30).

(Phenylphosphinous acid)pentacarbonyltungsten (3b). Complex **1b** (1.5 g, 2.3 mmol) was heated at 140 °C for 5.5 h in a sealed tube with distilled water (0.5 mL) in toluene–THF. After evaporation, the residue was chromatographed with toluene (R_f ~0.4): yield, 0.93 g (90%) of colorless oil; mass spectrum (chemical ionization, ^{184}W), m/e (relative intensity) 450 (M, 100).

(*N*-Phenylphenylphosphinamide)pentacarbonylchromium (4a). Complex **1a** (1.5 g, 2.9 mmol) was heated at 140 °C for 15 h in a sealed tube with aniline (1 mL, 11 mmol) in toluene. After evaporation, the residue was chromatographed with hexane–toluene (80:20): R_f ~0.5; yield, 0.5 g (45%) of colorless solid; mass spectrum (chemical ionization), m/e (relative intensity) 394 (M + 1, 100). Anal. Calcd for $C_{17}H_{12}CrNO_5P$: C, 51.92; H, 3.08; P, 7.88; N, 3.56. Found: C, 52.00; H, 3.08; P, 7.79; N, 3.52.

(*N*-Phenylphenylphosphinamide)pentacarbonyltungsten (4b). Complex **1b** (6.5 g, 10 mmol) was treated with aniline (3 mL, 33 mmol) in refluxing toluene (50 mL) for 6 h. After evaporation, the residue was chromatographed with hexane–toluene (90:10): R_f ~0.5; yield, 4 g (76%) of colorless solid; mp, 78 °C; mass spectrum (chemical ionization, ^{184}W), m/e (relative intensity) 526 (H + 1, 100). Anal. Calcd for $C_{17}H_{12}NO_5PW$: C, 38.88; H, 2.30; N, 2.67; P, 5.90. Found: C, 38.79; H, 2.20; N, 2.45; P, 5.92.

(*N*-Phenylmethylphosphinamide)pentacarbonyltungsten (4c). Complex **1c** (1.3 g, 2 mmol) was heated at 140 °C for 14 h in a sealed tube with aniline (1 mL, 11 mmol) in toluene. After evaporation, the residue was chromatographed with hexane–toluene (90:10): R_f ~0.5; yield, 0.13 g (15%) of colorless oil. Anal.

Table I. Spectral Data for [RP(H)A]M(CO)$_5$ Complexes

complex	^{1}H NMR[a]			^{31}P NMR[b]	IR[c]		remarks
	P–H	R	A		P–H	CO	
2a	6.96 (337.9)	7.0–7.16	2.80 (12.2)	158.5	2320	2070 m, 1950 vs	
2b	7.24 (346)	7.15	2.76 (12.5)	105.1	2335	2076 m, 1950 vs	
3a	7.31 (346.7)	7.03		137.1	2290	2068 m, 1945 vs	ν(OH) 3550–3300 br (in KBr)
3b	7.49 (355.7)	7.0	2.35 (br)	82.7 (271)	2300	2075 m, 1947 vs	ν(OH) 3530–3350 br (in KBr)
4a	6.82 (360.6)	6.22–7.24	4.33 (22) [NH]	61.06	2290	{2068 m, 1960 vs {1952 s, 1943 vs	{ν(NH) 3418 (KBr) {^3J(*H*N-P*H*) = 5.13
4b	7.08 (367.7)	6.2–7.2	4.32 (23) [NH]	12.07 (253.9)	2320	2075 m, 1950 vs	{ν(NH) 3410 (KBr) {^3J(*H*N-P*H*) = 5.13
4c	6.25 (363.5)	1.15 (5.61)	3.67 (20) [NH]	6.75 (249.0)	2320	{2075 m, 1957 s {1945 vs	{ν(NH) 3415 (KBr) {^3J(*H*N-P*H*) $\simeq$ ^3J(*H*P-C*H*$_3$) = 6.8
5	7.09 (354.2)	7.08	{0.75 [Me] {2.84 (12.4) [CH$_2$]	47.44 (253.9)		2070 m, 1945 vs	^3J(CH$_2$-*CH*$_3$) = 6.8
9	7.24 (370.4)	6.82–7.40		50.15 (273.4)	2360	{2080 m, 1968 s {1957 vs	
10	6.62 (365)	6.80–7.40		17.41 (268.5)	2370	{2080 m, 1968 s {1958 vs	
11	5.66 (357.7)	6.78–7.28		–54.24 (256.3)	2350	2080 m, 1957 vs	
12	6.67 (357.7)	7.0	1.31 (br)	16.28 (246.6)	2295	{2072 m, 1955 s {1945 vs	{ν(NH$_2$) 3440–3340 br (in KBr) {^3J(*H*P-NH$_2$) = 3.2
13	6.17 (367.9)	6.92		–1.78	2360	2073 w, 1960 vs	

[a] In C_6D_6 solution; δ in ppm; J(H–P) values (Hz) in parentheses. [b] In toluene solution; δ in ppm; ^1J(^{31}P–^{184}W) values (Hz) in parentheses. [c] ν in cm^{-1}; ν(P–H) recorded in KBr; ν(CO) recorded in decaline (only the main stretching frequencies are given); precision ±5 cm^{-1}.

Calcd for $C_{12}H_{10}NO_5PW$: C, 31.13; H, 2.18; N, 3.02. Found: C, 30.36; H, 2.27; N, 2.65.

(*N*,*N*-Diethylphenylphosphinamide)pentacarbonyltungsten (5). Complex **1b** (1.5 g, 2.3 mmol) was heated at 150 °C for 15 h in a sealed tube with diethylamine (2 mL, 19 mmol) in toluene. After evaporation, the residue was chromatographed with hexane–toluene (90:10): yield, 0.71 g (61%) of colorless oil. Anal. Calcd for $C_{15}H_{16}NO_5PW$: C, 35.67; H, 3.19; N, 2.77. Found: C, 35.84; H, 3.32; N, 2.66.

(*O*-Methyl methylphenylphosphinite)pentacarbonyltungsten (7). Complex **2b** (1.5 g, 3.2 mmol) was treated with potassium *tert*-butoxide (0.36 g, 3.2 mmol) in THF (50 mL). After 3 min at room temperature, methyl iodide (0.3 mL, 4 mmol) was added to the reaction mixture. After 1 h of stirring, KI was removed by filtration, THF was evaporated, and the residue was chromatographed with hexane–toluene (90:10): yield, 0.64 g (40%) of colorless oil; ^{1}H NMR (C_6D_6) δ 1.57 (d, ^2J(H–P) = 5.13 Hz, 3 H, MeP), 2.78 (d, ^3J(H–P) = 12.7 Hz, 3 H, MeO), 7.15 (m, Ph); ^{31}P NMR (toluene) δ 114.5 (^1J(^{183}W–^{31}P) = 278.3 Hz); IR (decalin) ν(CO) 2072 (w), 1985 (vw), 1955 (s), 1943 (vs), 1915 (vw) cm^{-1}; mass spectrum (^{184}W), *m/e* (relative intensity) 478 (M, 37), 450 (M – CO, 20), 422 (M – 2CO, 6), 394 (M – 3CO, 24), 366 (M – 4CO, 2), 338 (M – 5CO, 100). Anal. Calcd for $C_{13}H_{11}O_6PW$: C, 32.66; H, 2.32. Found: C, 32.90; H, 2.36.

[*O*-Methyl (diphenylhydroxymethyl)phenylphosphinite]pentacarbonyltungsten (8). Complex **2b** (1.2 g, 2.6 mmol) was treated with potassium *tert*-butoxide (0.3 g, 2.7 mmol) in THF. After 4 min at room temperature, benzophenone (0.5 g, 2.7 mmol) was added to the reaction mixture. After 30 min of stirring, water was added. After evaporation of the solvents, the residue was extracted with dichloromethane. The extract was purified by chromatography with hexane–toluene (90:10): R_f ~0.5; yield, 0.52 g (31%) of colorless solid; mp 110 °C; ^{1}H NMR (C_6D_6) δ 2.94 (d, ^3J(H–P) = 12.9 Hz, 3 H, MeO), 5.97 (d, ^3J(H–P) = 12.2 Hz, 1 H, OH), 6.93–7.62 (m, 15 H, Ph); ^{31}P NMR (toluene) δ 154.2 (^1J(^{183}W–^{31}P) = 332 Hz); IR (decalin) ν(CO) 2073 (w), 1985 (vw), 1956 (s), 1945 (vs); mass spectrum (chemical ionization with NH_3, ^{184}W), *m/e* (relative intensity) 664 (M + NH_4, 100), 646 (M, 12), 184 (Ph_2CHOH, 80), 167 (Ph_2CH 80). Anal. Calcd for $C_{25}H_{19}O_7PW$: C, 46.46; H, 2.96. Found: C, 46.47; H, 2.89.

(Phenylchlorophosphine)pentacarbonyltungsten (9). A stream of gaseous anhydrous HCl was bubbled for 5 min through a toluene solution of complex **2b** (toluene, 30 mL; **2b**, 1.2 g (2.4 mmol) at room temperature. The mixture then was cooled to 0 °C in order to allow a complete precipitation of the aniline hydrochloride. The precipitate was removed by filtration on paper. The toluene was evaporated. The residue was recrystallized from hexane: yield, 0.83 g (74%) of yellow solid; mp 55 °C; mass spectrum (^{35}Cl, ^{184}W), *m/e* (relative intensity) 468 (M, 18), 433 (M – Cl, 6), 412 (M – 2CO, 6), 384 (M – 3CO, 6), 356 (M – 4CO, 24), 328 (M – 5CO, 100). Anal. Calcd for $C_{11}H_6ClO_5PW$: C, 28.20; H, 1.29. Found: C, 28.01; H, 1.35.

(Phenylbromophosphine)pentacarbonyltungsten (10). The same procedure as for **9** was used, with HBr replacing HCl: yield from 1 g of **2b**, 0.9 g (89%) of yellow solid; mp 59 °C (hexane); mass spectrum (^{79}Br, ^{184}W), *m/e* (relative intensity) 512 (M, 70), 456 (M – 2CO, 30), 432 (M – Br, 22), 400 (M – 4CO, 17), 372 (M – 5CO, 100). Anal. Calcd for $C_{11}H_6BrO_5PW$: C, 25.76; H, 1.18; P, 6.04. Found: C, 26.53; H, 1.19; P, 6.19 (slight hydrolysis).

(Phenyliodophosphine)pentacarbonyltungsten (11). The same procedure as for **9** was used, with HI replacing HCl. HI was produced by reacting iodine with boiling tetralin[8] and was carried away by a stream of argon. As the HI stream was very dilute, the reaction with **2b** required longer time (30 min); yield from 1.1 g of **2b**, 1 g (81%) of yellow solid; mp 79 °C (hexane); mass spectrum (120 °C, ^{184}W), *m/e* (relative intensity) 560 (M, 25), 532 (M – CO, 3), 504 (M – 2CO, 10), 476 (M – 3CO, 3), 448 (M – 4CO, 20), 433 (M – I, 58), 420 (M – 5CO, 42), 405 (433 – CO, 13), 377 (433 – 2CO, 45), 349 (433 – 3CO, 61), 321 (433 – 4CO, 38), 293 (433 – 5CO, 100). This compound was not very stable and was not analyzed.

(Phenylphosphinamide)pentacarbonyltungsten (12). A stream of gaseous anhydrous ammonia was bubbled for 1 h

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through a toluene solution of complex **9** (1.2 g, 2.6 mmol) at room temperature. After filtration, toluene was evaporated and the residue was chromatographed with hexane–toluene (60:40): R_f ~0.4; yield, 0.82 g (69%) of colorless solid; mp 68 °C; mass spectrum (^{184}W), m/e (relative intensity) 449 (M, 91), 421 (M – CO, 31), 393 (M – 2CO, 31), 365 (M – 3CO, 14), 337 (M – 4CO, 34), 309 (M – 5CO, 100). Anal. Calcd for $C_{11}H_8NO_5PW$: C, 29.43; H, 1.79; N, 3.12; P, 6.90. Found: C, 29.74; H, 1.32; N, 2.79; P, 6.80.

Bis[(phenylphosphido)pentacarbonyltungsten] Sulfide (13). Complex **9** (1 g, 2.1 mmol) was treated with anhydrous NaSH (0.28 g, 5 mmol) in toluene at room temperature for one night. After filtration and evaporation the residue was chromatographed with hexane–toluene (90:10): R_f ~0.5; yield 0.41 g (43%) of colorless solid; mp 157 °C (hexane–toluene); mass spectrum (chemical ionization with NH_3, ^{184}W), m/e 914 (relative intensity) (M + NH_2, 100), 899 (M + 1, 16). There was no SH stretch on the IR spectrum around 2550 cm^{-1}.

Dismutation of Complex 9. Complex **9** (2 g, 4.2 mmol) was treated with $AlCl_3$ (0.6 g, 4.5 mmol) in dichloromethane for 3 h at room temperature. After hydrolysis, the organic phase was evaporated. The organic residue was chromatographed with hexane. The first recovered product (R_f ~0.8) was (phenyldichlorophosphine)pentacarbonyltungsten (**15**): yield 38%; mass spectrum (70 eV, ^{35}Cl, ^{184}W), m/e 502 (M, 90), 467 (M – Cl, 66), 362 (M – 5CO, 100), 327 (362 – Cl, 50); ^{31}P NMR (hexane) δ 126.2 ($^1J(^{183}W-^{31}P)$ = 341.8 Hz); IR (decalin) ν(CO) 2084 (w), 1978 (s), 1967 (vs) cm^{-1}. The second product (R_f ~0.4) was (phenylphosphine)pentacarbonyltungsten (**14**): yield, 44%; ^1H NMR (C_6D_6) δ 4.77 (d, ^1J(H–P) = 343 Hz, 1 H, PH), 6.91–7.16 (m, 5 H, Ph); ^{31}P NMR (hexane) δ –87.7 ($^1J(^{183}W-^{31}P)$ = 224.6 Hz) (these NMR data are very similar to those reported in the literature for this compound[9]); IR (decalin) ν(CO) 2077 (w), 1948 (vs) cm^{-1}; KBr ν (PH) 2325 cm^{-1}. An easy dismutation of **14** seemed to occur in the mass spectrometer (electronic impact, 70 eV, ^{184}W): $(PhPH_2)_2W(CO)_4$ was thus obtained (m/e 516). Both complexes (**14** and **15**) have been already described in the literature.[9,10]

Registry No. 1a, 82265-63-2; **1b**, 82265-64-3; **1c**, 82265-65-4; **2a**, 82839-06-3; **2b**, 82265-66-5; **3a**, 82839-07-4; **3b**, 82839-08-5; **4a**, 82839-09-6; **4b**, 82839-10-9; **4c**, 82839-11-0; **5**, 82839-12-1; **7**, 82839-13-2; **8**, 82839-14-3; **9**, 82839-15-4; **10**, 82839-16-5; **11**, 82839-17-6; **12**, 82839-18-7; **13**, 82839-19-8; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; NaSH, 16721-80-5; $AlCl_3$, 7446-70-0; (1-phenyl-3,4-dimethylphosphole)pentacarbonylchromium, 74363-90-9; dimethyl acetylenedicarboxalate, 762-42-5; (1-phenyl-3,4-dimethylphosphole)pentacarbonyltungsten, 74363-95-4; (1,3,4-trimethylphosphate)pentacarbonyltungsten, 82849-01-2; methanol, 67-56-1; water, 7732-18-5; aniline, 62-53-3; diethylamine, 109-89-7; methyl iodide, 74-88-4; benzophenone, 119-61-9; ammonia, 7664-41-7.

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Intramolecular In–N Coordination. Synthesis and NMR Study of Four-Coordinate $[2\text{-}Me_2NCH(Z)C_6H_4]Me_2In$ and Five-Coordinate $[2\text{-}Me_2NCH(Z)C_6H_4]_2InCl$ (Z = H or (*S*)-CH_3)

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Arylindium compounds of the type Ar_2InCl and $ArMe_2In$, in which the Ar group is either 2-$Me_2NCH_2C_6H_4$ or (*S*)-2-$Me_2NCH(Me)C_6H_4$, have been synthesized by the organolithium route and characterized by ^1H and ^{13}C NMR spectroscopy. The NMR results clearly reveal that intramolecular In–N coordination occurs in solution, resulting in five-coordinate Ar_2InCl and four-coordinate $ArMe_2In$ structures. In pyridine solution, the In–N bond in the four-coordinate $ArMe_2In$ compounds weakens as the result of the formation of a five-coordinate intermediate in which the NMe_2 and pyridine ligand are in axial positions.

Introduction

There has recently been considerable interest in the structural properties of organoindium(III) compounds and their derivatives, and X-ray crystallographic and other studies have revealed a variety of coordination numbers and stereochemistries at the indium atom. Distorted trigonal-bipyramidal geometry is found in a number of compounds in which intermolecular coordination takes place, including $[(CH_3)_2InCl]_2$,[1] $[CH_3InCl_2]_2$,[2] $(C_2H_5)_2InOSCCH_3$,[3] and $[(CH_3)_2In(ON{=}CHC_5H_4N)_2]_2$.[4] The triorganoindium(III) compounds $(CH_3)_3In$[5] and $(C_6H_5)_3In$[6] also involve five-coordinate indium in the solid state, although $(CH_3)_3In$ is a trigonal-planar monomer in the gas phase,[7,8] and both compounds are monomeric in various

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