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METAL CARBONYL COMPLEXES OF PHENYLPHOSPHINE AND DIPHENYLPHOSPHINE

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SUMMARY

Reactions of various metal carbonyls or their derivatives and diphenylphosphine (L) or phenylphosphine (L′) lead exclusively to ligand (carbonyl or halide) replacement; the following complexes are reported: $[C_5H_5Fe(CO)_2L]Br$, $[C_5H_5Fe(CO)_2L']I$, $[C_5H_5Mo(CO)_3L]PF_6$, $C_5H_5Mo(CO)_2LCl$, $Mn(CO)_3L_2Br$, $Mn(CO)_3L'_2Br$, $Mn(CO)_4LBr$, $Mn(CO)_4L'Br$, $Mn(CO)_4(L)C_6H_5$, $Cr(CO)_4L'_2$, $Mo(CO)_3L'_3$. Deprotonations of several of these species using n-butyllithium or sodium methoxide (cations only) were carried out and reactions of the resulting species studied. Reactions of deprotonated species included alkylation by methyl iodide to give methylphenylphosphine complexes, dimerization via μ-phosphido groups with CO loss, and intramolecular rearrangements. In the latter category we observe that $[C_5H_5Fe(CO)_2P(C_6H_5)Li_2]PF_6$ rearranges to give $C_5H_5Fe(CO)_2Li$ and $LiPF_6$, and $Mn(CO)_4[P(C_6H_5)_2Li]Br$ and $C_5H_5Fe(CO)[P(C_6H_5)_2Li]Br$ eliminate LiBr to give $[Mn(CO)_4P(C_6H_5)_2]_2$ and $[C_5H_5Fe(CO)P(C_6H_5)_2]_2$ respectively. Finally, we have irradiated $M(CO)_5PR_2H$ and $M(CO)_5PR_2Li$ species ($M=Cr$, Mo, W; $R=C_6H_5$) and observe that dimerization with accompanying oxidation to give $M_2(CO)_8(PR_2)_2$ and ligand redistribution to $M(CO)_4(PR_2H)_2$ are often seen; the former reaction occurs more often with the lithio species.

INTRODUCTION

Few reactions of metal carbonyls with primary or secondary phosphines have been reported. Hieber and coworkers[1] described reactions of various phosphines (R_2PH, RPH_2, PH_3) and vanadium carbonyl which give dimeric complexes containing bridging phosphido groups. A number of reactions of the iron carbonyls with secondary phosphines are reported, giving $Fe(CO)_4PR_2H$[2], $Fe(CO)_3(PR_2H)_2$[2], $Fe_2(CO)_6(PR_2)_2$[3,4] or $Fe_2(CO)_6[P(CF_3)_2]_2H_2$[4], the product depending on reaction conditions and on the phosphine chosen. Several secondary phosphine complexes of the chromium group carbonyls have also been prepared[2,5].

The number of metal carbonyl reactions with primary and secondary phosphines seems remarkably small, especially in view of the extensive study accorded to complexes of tertiary phosphines[6], and even in comparison to reactions with phosphine itself[7]. However, it is fair to say that the anticipated reactions of these species are usually observed. Using moderate conditions the most common reaction of a metal carbonyl and a primary or secondary phosphine is carbonyl replacement[2,5]. Hydrogen loss, giving complexes with bridging phosphido groups, generally occurs when more forcing conditions are employed[3,4]. It may be observed that these reactions are considerably less facile than reactions of metal carbonyls with mercaptans and with H_2S, which invariably involve hydrogen loss[8].

We recently described[9] studies on reactions of iron carbonyls with mono- and diorganophosphines, which supported this pattern of behavior. With phenylphosphine, one obtains $Fe(CO)_4(C_6H_5PH_2)$, $Fe_2(CO)_6(C_6H_5PH)_2$ or $Fe_3(CO)_9(PC_6H_5)_2$ depending on the reaction temperature. With secondary phosphines both $Fe(CO)_4(PR_2H)$ and $Fe_2(CO)_6(PR_2)_2$ are formed; in addition, a new hydroxide bridged complex, $Fe_2(CO)_6(PR_2)OH$, is obtained in small yield. The latter complexes are prepared in better yield from reactions of the deprotonated complex, $[Fe(CO)_4PR_2Li]$ [obtained from $Fe(CO)_4(PR_2H)$ and n-butyllithium], and $Fe_2(CO)_9$[10].

In this paper we describe further work with primary and secondary phosphine complexes of various metal carbonyls, directed toward syntheses of complexes of these ligands and study of their reactions.

EXPERIMENTAL

Various starting materials, including $C_5H_5Fe(CO)_2Br$[11], $C_5H_5Fe(CO)_2I$[11], $Mn(CO)_5Br$[11], $Mn_2(CO)_8Br_2$[12], $Mn(CO)_5C_6H_5$[13], (norbornadiene)$Mo(CO)_4$[11], $C_5H_5Mo(CO)_3Cl$[14], $M(CO)_5P(C_6H_5)_2H$ (M=Cr, Mo, W)[2], $P(C_6H_5)_2H$[15] and $C_6H_5PH_2$[16] were prepared as described in the literature. Phenylphosphine has a particularly unpleasant odor; extra care must be taken in its handling[9].

Infrared spectra were recorded on Beckman IR-10 and Perkin Elmer 421 spectrophotometers. The low resolution data from 3500–400 cm^{-1}, were obtained using a combination of Nujol and Fluorolube mulls for solids and thin films for liquids, except as noted otherwise in the manuscript. Proton NMR data were obtained using Varian A-60A and XL-100 instruments. Molecular weights were determined by mass spectroscopy (AEI MS-902) when possible, or by osmometry using a Mechrolab osmometer and benzene solutions of about 0.01 molal. Analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee. n-Butyllithium was standardized by the Gilman double-titration method[17]. All reactions were carried out under a nitrogen atmosphere.

Ultraviolet irradiation reactions were conducted in Pyrex flasks using a General Electric H 100-PSP44-4 Mercury lamp powered by a Hanovia #31350-4 transformer.

Synthesis of phosphine complexes

Reaction of $C_5H_5Fe(CO)_2Br$ and $P(C_6H_5)_2H$. A 25.0 g sample of $C_5H_5Fe(CO)_2Br$ (97.0 mmol) and 18.6 g $P(C_6H_5)_2H$ (100 mmol) were stirred in 500 ml benzene in the dark for 7 days. The insoluble $[C_5H_5Fe(CO)_2P(C_6H_5)_2H]Br$ was separated by filtration from the green filtrate. The solid was dissolved in warm water, filtered, and an excess of NH_4PF_6 in water was added. The iron complex, now as the PF_6^- salt, was filtered and crystallized from acetone/water, giving the product as golden yellow crystals. Yield 42.5 g, 85%; m.p., 180–182°. (Found: C, 45.1; H, 3.21; P, 12.3. $C_{19}H_{16}F_6FeO_2P_2$ calcd.: C, 45.0, H, 3.15; P, 12.2%.)

Infrared (in CH_2Cl_2): ν(CO) 2065 s, 2019.5 s cm^{-1}; ν(P–H), not observed; other bands: 1703 m, 1481 m, 1335 m, 854 w, 820 vs, 751 w, 745 w, 736 w, 697 w, 610 m, 579 m, 560 w, 510 m cm^{-1}.

NMR (in acetone-d_6): τ 2.36, multiplet, C_6H_5; τ 2.39, doublet, J(P–H) 410 Hz, PH; τ 4.32, doublet, J(P–H) 2 Hz, C_5H_5.

The green filtrate from the original reaction was evaporated and the residue chromatographed on a Florisil column using benzene as an eluant. A small red band eluted first; this was identified as $[C_5H_5Fe(CO)_2]_2$ from its infrared spectrum. A green band was then eluted with 1/1 benzene/acetone; evaporation gave an unstable green oil. This could not be purified, and was identified by its infrared and NMR spectra as $C_5H_5Fe(CO)[P(C_6H_5)_2H]Br$ (0.68 g, 1.7%).

Infrared (in CH_2Cl_2): ν(CO), 1961 s (br) cm^{-1}; ν(P–H), not observed; other bands: 1700 m (br), 1595 w, 1485 w, 1440 m, 1267 m, 1183 w, 1118 w, 1093 m, 1002 w, 827 w, 937 s, 895 s, 560 s, 530 s, 520 s cm^{-1}.

NMR (in $CDCl_3$): τ 2.56, multiplet, C_6H_5; τ 4.07, doublet J(P–H) 367 Hz, PH; τ 5.44, singlet, C_5H_5.

Reaction of $C_5H_5Fe(CO)_2I$ and $C_6H_5PH_2$. Phenylphosphine (10.0 g, 90 mmol) and $C_5H_5Fe(CO)_2I$ (27.5 g, 90 mmol) were refluxed in 150 ml benzene for 22 h. The resulting solid $[C_5H_5Fe(CO)_2P(C_6H_5)H_2]I$ was converted to the hexafluorophosphate salt and purified as described above, giving yellow, light sensitive crystals. Yield 5.1 g, 13%; m.p. 187–191°. (Found: C, 36.3; H, 2.64; P, 14.2. $C_{13}H_{12}F_6FeO_2P_2$ calcd.; C, 37.1, H, 2.78; P, 14.3%.)

Infrared (in acetonitrile): ν(CO), 2038 s, 2016 s cm^{-1}; ν(P–H), not observed; other bands: 890 (sh), 870 m, 845 s, 740 m, 692 m, 620 m, 580 m, 560 s cm^{-1}.

NMR (in acetone-d_6): τ 2.62, multiplet, C_6H_5; τ 4.62, singlet, C_5H_5; τ 6.87, doublet, J(P–H) 3.78 Hz, PH_2.

The green compound $C_5H_5Fe(CO)(C_6H_5PH_2)I$ was worked up in the same manner as described above, but it was also unstable, and was characterized by its infrared spectrum only.

Infrared: ν(CO), 1965 cm^{-1}; ν(P–H), 2340 w cm^{-1}; other bands: 2970 w, 1720 w, 1640 w, 1440 w, 1080 s, 1030 s, 880 m, 800 m, 560 m, 530 m cm^{-1}.

NMR (in $CDCl_3$): τ 2.61, multiplet, C_6H_5; τ 5.45, singlet, C_5H_5; PH_2 not observed.

Preparation of $[C_5H_5Mo(CO)_3P(C_5H_5)_2H]PF_6$. A solution of 5.6 g $C_5H_5Mo(CO)_3Cl$ (19.7 mmol) and 4.2 g $AlCl_3$ (31.4 mmol) were stirred in 200 ml benzene for $\frac{1}{2}$ h; then 3.65 g $P(C_6H_5)_2H$ (19.7 mmol) was added. The mixture was stirred overnight. Solvent was removed and the residue extracted with warm water until the extracts were colorless. The water solution was filtered and aqueous NH_4PF_6 was added. The resulting precipitate was filtered and recrystallized from methanol/acetone yielding the product as yellow needles. Yield 2.5 g, 22%; m.p., 188–190°. (Found: C, 41.8; H, 2.74; P, 10.5. $C_{18}H_{16}F_6MoO_3P_2$ calcd.: C, 41.7; H, 2.70; P, 10.8%.)

Infrared (in CH_2Cl_2): ν(CO), 2166 s, 2006 w, 1975 s cm^{-1}; ν(P–H), 2420 vw cm^{-1}; other bands: 1590 w, 1579 w, 1481 w, 1440 m, 1425 m, 1312 w, 1189 w, 1100 m, 1072 w, 1029 w, 1010 w, 1000 w, 927 w, 820 vs (br), 740 s, 692 s, 555 s, 540 s, 495 s, 482 s, 465 (sh), 453 s, 420 m cm^{-1}.

NMR (in acetone-d_6): τ 2.26, doublet, J(P–H) 413 Hz, PH; τ 2.39, multiplet, C_6H_5; τ 3.97, singlet, C_5H_5.

Preparation of $C_5H_5Mo(CO)_2[P(C_6H_5)_2H]Br$. A solution of 13.0 g $C_5H_5Mo(CO)_3Br$ (40 mmol) and 7.47 g $P(C_6H_5)_2H$ (40 mmol) in 500 ml benzene was stirred for six weeks. The solvent was then evaporated and the residue was dissolved in chloroform and chromatographed on a Florisil column. The orange band of the product eluted with chloroform. Heptane was added to the solution of the product in chloroform; evaporation then yielded the product as orange crystals. Yield 8.1 g, 42%; m.p., 172–174°. (Found: C, 47.3; H, 3.57; P, 6.36; mol. wt., 450. $C_{19}H_{16}BrMoO_2P$ calcd.: C, 47.2; H, 3.32; P, 6.42%; mol. wt., 483.)

Infrared (in CH_2Cl_2): ν(CO), 1971.5 s, 1879.5 s cm^{-1}; ν(P–H), 2335 w cm^{-1}; other bands: 1483 m, 1436 m, 1420 w, 1309 w, 1180 w, 1094 w, 1066 w, 1011 w, 927 w, 897 m, 857 m, 820 m, 738 m, 693 m, 588 w, 546 m, 520 m, 502 m, 488 m, 463 w, 447 m cm^{-1}.

NMR (in $CDCl_3$): τ 2.61, multiplet, C_6H_5: τ 2.86, doublet, J(P–H) 375 Hz, PH; τ 4.73, singlet C_5H_5.

Reaction of $Mn(CO)_5Br$ and $C_6H_5PH_2$. A solution of 3.0 g $Mn(CO)_5Br$ (10.7 mmol) and 1.1 g $C_6H_5PH_2$ (10 mmol) in 80 ml benzene was refluxed for 38 h. The reaction mixture was then evaporated to an oil, dissolved in chloroform, filtered, and evaporated. The residue was dissolved in benzene and chromatographed on Florisil. After two minor components (not identified) eluted, a larger third fraction was collected. This was evaporated and the residue recrystallized from dichloromethane/hexane to yield yellow crystals of $Mn(CO)_4(C_6H_5PH_2)Br$. Yield 0.1 g, 2.6%; m.p. 100–102°. (Found: C, 33.7; H, 1.98; P, 8.57; mol.wt., 366. $C_{10}H_7BrMnO_4P$ calcd.: C, 33.6; H, 1.96; P, 8.70%; mol.wt., 357.)

Infrared (in CH_2Cl_2): ν(CO), 2085 s, 2010 s, 1971 s (br) cm^{-1}; ν(P–H), not observed, other bands (CH_2Cl_2): 1485 vw, 1438 vw, 872 m, 648 m, 620 s cm^{-1}.

NMR: τ 2.34, multiplet, C_6H_5; τ 4.04, doublet, J(P–H) 358 Hz, PH_2.

The fourth band eluted from the column with chloroform. This compound, $Mn(CO)_3(C_6H_5PH_2)_2Br$, was purified by crystallization from dichloromethane/hexane. Yield 0.2 g, 5.2%; m.p. 85–87°. (Found: C, 40.2; H, 3.21; P, 13.4; mol. wt., 470. $C_{15}H_{14}BrMnO_3P_2$ calcd.: C, 41.0; H, 3.19; P, 14.1%; mol. wt., 439.)

Infrared (in CH_2Cl_2): ν(CO), 2030 s, 1975 s(br), 2010 m, 1950 s(br) cm^{-1}; ν(P–H), not observed; other bands (CH_2Cl_2): 1485 w, 1439 m, 870 m, 658 m, 628 m, 610 m, 550 w, 530 w cm^{-1}.

NMR (in $CDCl_3$): τ 2.80, multiplet, C_6H_5; the PH_2 resonances were not located due to low solubility.

Reaction of $Mn(CO)_5Br$ and $P(C_6H_5)_2H$. A solution of 16.1 g $Mn(CO)_5Br$ (58.6 mmol) and 10.8 g $P(C_6H_5)_2H$ (58.0 mmol) in 400 ml of dichloromethane was stirred for 3 h; during this time gas evolution was observed. Solvent was removed and the residue recrystallized from chloroform/hexane giving orange crystals of $Mn(CO)_4[P(C_6H_5)_2H]Br$. Yield 8.3 g, 33%; m.p. 129°. (Found: C, 44.1; H, 2.61; P, 7.15; mol. wt., 440. $C_{16}H_{11}BrMnO_4P$ calcd.: C, 43.3; H, 2.48; P, 7.00%; mol. wt., 433.)

Infrared (in heptane): ν(CO), 2097 w, 2031 m, 2020 s, 1960.5 m cm^{-1}. ν(P–H), not observed; other bands: 1481 m, 1435 m, 1090 w, 1020 w, 960 w, 898 m, 881 m, 741 m, 731 s, 686 m, 648 m, 623 m, 606 s cm^{-1}.

NMR (in $CDCl_3$): τ 2.56, multiplet, C_6H_5; τ 3.17, doublet, J(P–H) 374 Hz, PH.

In other similar reactions, mixtures of $Mn(CO)_5Br$, $Mn(CO)_4[P(C_6H_5)_2H]Br$ and $Mn(CO)_3[P(C_6H_5)_2H]_2Br$ were obtained which were difficult to separate.

Reaction of $Mn_2(CO)_8Br_2$ *and* $P(C_6H_5)_2H$. It was hoped that this reaction would provide a good route to $Mn(CO)_4[P(C_6H_5)_2H]Br$, but this did not prove to be the case. A mixture of 12.4 g $Mn_2(CO)_8Br_2$ (25.1 mmol) and 9.21 g $P(C_6H_5)_2H$ (50 mmol) in 500 ml dichloromethane was stirred for 21 h. Solvent was removed and the residue crystallized from dichloromethane/hexane to give orange crystals of $Mn(CO)_3[P(C_6H_5)_2H]_2Br$. Yield 4.5 g, 30%; m.p. 148–149°. (Found: C, 55.0%; H, 3.80; P, 10.6; mol. wt., 586. $C_{27}H_{22}BrMnO_3P_2$ calcd.: C, 54.8; H, 3.72; P, 10.5%; mol. wt., 591.)

Infrared (in heptane): ν(CO), 2039 s, 1974 s, 1918 s cm^{-1}; ν(P–H), 2310 w cm^{-1}; other bands: 1586 w, 1570 vw, 1481 m, 1432 m, 1190 m(br), 1121 w, 1098 w, 1022 w, 940 w(br), 929 w, 886 m, 860 m, 846 m, 727 s, 686 s, 653 m, 627 m, 604 m cm^{-1}.

NMR (in $CDCl_3$): τ 2.56, multiplet, C_6H_5; τ 3.17, doublet, J(P–H) 374 Hz, PH.

Preparation of $C_6H_5Mn(CO)_4[P(C_6H_5)_2H]$. A solution of 17.2 g $C_6H_5COMn(CO)_5$ (57.4 mmol) was refluxed in 1000 ml ethyl ether for 16 h, at which time complete decarbonylation to $C_6H_5Mn(CO)_5$ had taken place. Then 10.45 g $P(C_6H_5)_2H$ were added and the mixture allowed to stand for 6 h and then refluxed for 18 h. The solution was reduced in volume to 200 ml, filtered, and then was slowly chilled to −78°. The product, $C_6H_5Mn(CO)_4[P(C_6H_5)_2H]$ separated slowly; it was filtered off and recrystallized. Yield 4.7 g, 19%; m.p., 93°. (Found: C, 60.6; H, 3.75; P, 7.17; mol. wt., 450. $C_{22}H_{16}MnO_4P$ calcd.: C, 61.4; H, 3.72; P, 7.22%; mol. wt., 430.)

Infrared (in heptane): ν(CO), 2073.5 s, 2004 s, 1984 s(br), 1975 s(br) cm^{-1}; ν(P–H), 2340 cm^{-1}; other bands: 1562 m, 1469 m, 1432 m, 1417 w, 1385 w, 1300 w, 1190 m(br), 1116 w, 1087 w, 1060 w, 1020 w, 994 m, 960 w, 919 w, 906 w, 890 w, 865 m, 837 w, 730 m, 724 m, 683 m, 630 s cm^{-1}.

NMR (in C_6D_6): τ 2.62, multiplet, $(C_6H_5)_2P$; τ 2.94, multiplet, C_6H_5Mn; τ 3.79, doublet, J(P–H) 371 Hz, PH.

Preparation of $Cr(CO)_4(C_6H_5PH_2)_2$. A solution of 5.0 g $Cr(CO)_6$ (22.7 mmol) in 200 ml acetonitrile was refluxed for 13 h giving $Cr(CO)_3(CH_3CN)_3$[18]. To this solution was added 5.0 g $C_6H_5PH_2$ (45.5 mmol) and the solution was refluxed for ½ h then irradiated with an ultraviolet lamp for 1 h. The solvent was evaporated, and the resulting oil dissolved in hexane and chromatographed on Florisil. One band (colorless) was collected, eluting with 1/1 hexane/benzene. This material obtained on evaporation was recrystallized from heptane at −78° to give pale green crystals of $Cr(CO)_4(C_6H_5PH_2)_2$. Yield 0.25 g, 3%; m.p., 51–52°. (Found: C, 49.9; H, 4.05; P, 16.2; mol. wt., 368. $C_{16}H_{14}CrO_4P_2$ calcd.: C, 50.0, H, 3.65; P, 16.2%; mol. wt., 386.)

Infrared (in heptane): ν(CO), 2023 s, 1939 s, 1918 vs cm^{-1}; ν(P–H), 2360 w cm^{-1}; other bands: 1499 w, 1432 w, 1079 w, 1071 w, 964 vw, 917 w, 880 m, 729 m, 715 w(sh), 685 m, 663 m, 642 s cm^{-1}.

NMR (in $CHCl_3$): τ 2.64, broad singlet, C_6H_5; τ 4.72, doublet J(P–H) 332 Hz, PH.

Preparation of $Mo(CO)_3(C_6H_5PH_2)_3$. A mixture of 5.1 g (norbornadiene)$Mo(CO)_4$ (17 mmol) and 3.8 g $C_6H_5PH_2$ (34.5 mmol) was refluxed in 70 ml methylcyclohexane for 6 h. The solvent was then removed and the residue was chromatographed on alumina, eluting with benzene. Only one band was seen. This was evaporated and the residue recrystallized from acetone/water giving the white crystalline product. Yield 0.40 g, 7%; m.p. 104–105°. (Found: C, 49.6; H, 4.12; P, 18.3; mol. wt., 524. $C_{21}H_{21}MoO_3P_3$ calcd.: C, 49.5; H, 4.12; P, 18.2%; mol. wt., 510.)

Infrared (in $CHCl_3$): ν(CO), 1962 s, 1872 s(br) cm^{-1}; ν(P–H), 2295 vw cm^{-1}; other bands: 1482 w, 1434 w, 1200 vw, 1082 w, 1062 vw, 967 w, 911 vw, 881 m, 850 w(sh), 735 m, 722 m, 687 m, 604 m, 585 w cm^{-1}.

NMR: τ 2.67, broad singlet, C_6H_5; τ 4.72, two indistinct multiplets (doublets?), J(P–H) 326 Hz, PH_2.

Deprotonation reactions of several metal carbonyl phosphine complexes

$[C_5H_5Fe(CO)_2C_6H_5PH_2]PF_6$. A 2.5 g sample of this compound (5.8 mmol) was stirred in ethyl ether and 4.0 ml of 1.5 M CH_3Li in ether was added dropwise. Gas (235 ml) was evolved (27°, 760 mmHg) *vs.* 286 ml expected for two equivalents of gaseous products (CH_4+CO). The resulting red solution was evaporated, and the residue chromatographed on alumina using chloroform as an eluant. A small amount of $[C_5H_5Fe(CO)_2]_2$, identified by its infrared spectrum, was first obtained. Then a second red band was eluted with dichloromethane. After evaporation, crystallization was accomplished from dichloromethane/ethyl ether, giving a red powder identified as $[C_5H_5Fe(CO)C_6H_5PH]_2$. Yield 0.3 g, 20%; m.p., 125–130° (dec.) (Found: C, 55.1; H, 3.87; Fe, 21.9; P, 12.0; mol. wt., 526. $C_{24}H_{22}Fe_2O_2P_2$ calcd.: C, 55.3; H, 4.26; Fe, 21.7; P, 12.0%; mol. wt., 516.)

Infrared (in CH_2Cl_2): ν(CO), 2010 m, 1980 m, 1970 (sh), 1950 m(br), 1930 (sh) cm^{-1}; ν(P–H), 2330 vw cm^{-1}, other bands (CH_2Cl_2): 905 m, 840 s, 615 w, 575 w, 555 m, 482 s cm^{-1}.

NMR (in $CDCl_3$): τ 2.65, multiplet, C_6H_5; τ 5.00, τ 5.20, multiplets, C_5H_5 (several isomers); no PH resonance was observed.

$[C_5H_5Fe(CO)_2\{P(C_6H_5)_2H\}]PF_6$. Solid sodium methoxide (0.85 g, 15.72 mmol) was added to a solution of 4.00 g $[C_5H_5Fe(CO)_2P(C_6H_5)_2H]PF_6$ (7.86 mmol) in 250 ml acetone. The mixture was refluxed, while the infrared spectrum was monitored to determine the extent of the reaction. After 36 h the solvent was evaporated and the residue was dissolved in benzene and chromatographed on alumina. The single band obtained was evaporated and a solid obtained which could be recrystallized from dichloromethane/hexane. It was shown by its infrared spectrum to be a mixture of *cis-* and *trans-*$[C_5H_5Fe(CO)P(C_6H_5)_2]_2$[19], 1.20 g, 46% yield. Careful chromatography by the literature method[19] separated the isomers in this sample; the product mixture was 74% *trans*, 26% *cis*.

$[C_5H_5Mo(CO)_3\{P(C_6H_5)_2H\}]PF_6$. Sodium methoxide (0.36 g, 6.60 mmol) was added to 1.90 g $[C_5H_5Mo(CO)_3\{P(C_6H_5)_2H\}]PF_6$ (3.30 mmol) in 50 ml acetone. The solution was stirred at room temperature for 24 h and filtered. The solvent was removed and the residue chromatographed on alumina. A 4/1 hexane/chloroform mixture eluted $[C_5H_5Mo(CO)_3]_2$. Yield 0.14 g, 17.6%. A second red band eluted with 1/1 hexane/chloroform; the amount of material obtained was too small to identify.

$[C_5H_5Fe(CO)_2(C_6H_5PH_2)]PF_6$. A suspension of 0.16 g (0.37 mmol) $[C_5H_5Fe(CO)_2(C_6H_5PH_2)]PF_6$ in 50 ml tetrahydrofuran at −78° was deprotonated with 0.55 ml of 1.355 M n-butyllithium. Methyl iodide (10 ml) was added and the mixture was added to 1.90 g $[C_5H_5Mo(CO)_3\{P(C_6H_5)_2H\}]PF_6$ (3.30 mmol) in 50 ml acetone. crystalline $[C_5H_5Fe(CO)_2\{P(CH_3)_2C_6H_5\}]PF_6$, was worked up as described above; 0.033 g, 19% yield; m.p., 157–158°. It was identified by comparison of m.p. and infrared data with that of a known sample.

The reaction with methyl iodide took a different course if the deprotonated species was warmed to room temperature first. In a typical reaction the lithio complex was formed from 1.68 g $[C_5H_5Fe(CO)_2(C_6H_5PH_2)]PF_6$ (3.90 mmol) and 5.76 ml of 1.355 *M* n-butyllithium at $-78°$. The mixture was warmed to room temperature and stirred for 36 h; then 15 ml of methyl iodide was added. After stirring for 18 h the solvent was removed and the residue extracted with 9/1 pentane/dichloromethane, and the extracts chromatographed over alumina. A single yellow band eluted with this solvent mixture. The product obtained after evaporation was identified as $C_5H_5Fe(CO)_2CH_3$ by its infrared[14] and NMR spectra[11]. Yield 0.40 g, 54%.

$[C_5H_5Fe(CO)_2\{P(C_6H_5)_2H\}]PF_6$. A 2.00 g (3.9 mmol) sample of $[C_5H_5Fe(CO)_2\{P(C_6H_5)_2H\}]PF_6$ was dissolved in 100 ml acetone and 0.425 g (8.86 mmol) sodium methoxide was added. After stirring (5 min) 10 ml methyl iodide was added; stirring was continued for 30 min. The solvent was then removed and the residue triturated with a conc. NH_4PF_6 solution; the solid was filtered and recrystallized from acetone on addition of ethyl ether. The product $[C_5H_5Fe(CO)_2\{P(C_6H_5)_2CH_3\}]PF_6$, 1.05 g, 51% yield, was obtained as yellow crystals, m.p. 177–178°. (Found: C, 45.9; H, 3.44. $C_{20}H_{18}F_6FeO_2P_2$ calcd.: C, 46.1; H, 3.53%.)

Infrared (in acetone): ν(CO), 2053 s, 2009 s cm^{-1}; other bands: 1588 vw, 1573 w, 1483 m, 1438 s, 1420 m, 1414 m, 1362 vw, 1337 vw, 1314 w, 1296 w, 1188 vw, 1160 w, 1115 vw, 1097 s, 1067 m, 1117 vw, 996 m, 952 vw, 927 vw, 887 s, 863 (sh), 835 vs (PF_6^-), 759 w, 740 s, 692 s, 598 s, 575 s, 546 s cm^{-1}.

NMR: τ 2.39, multiplet, C_6H_5; τ 4.32, doublet, *J*(P–H) 1.0 Hz, C_5H_5; τ 7.42, doublet, *J*(P–CH) 11.2 Hz, CH_3.

$[C_5H_5Mo(CO)_3\{P(C_6H_5)_2H\}]PF_6$. The reaction of 0.50 g (0.87 mmol) $[C_5H_5Mo(CO)_3\{P(C_6H_5)_2H\}]PF_6$ and 0.094 g (1.74 mmol) sodium methoxide in 25 ml acetone was carried out, and 5 ml methyl iodide added. The reaction was worked up as described above, to give 0.20 g, 39% yield, of yellow crystalline $[C_5H_5Mo(CO)_3\{P(C_6H_5)_2CH_3\}]PF_6$, m.p. 206–207°. (Found: C, 42.9; H, 3.14. $C_{21}H_{18}F_6MoO_3P_2$ calcd.: C, 42.7; H, 3.05%.)

Infrared (in acetone): ν(CO), 2060 s, 1996 (sh), 1965 s cm^{-1}; other bands: 1438 w, 1430 w, 1419 vw, 1304 vw, 1190 vw, 1163 vw, 1150 vw, 1097 w, 1088 w, 893 m, 858 m, 840 m, 825 s (PF_6^-), 749 w, 732 w, 718 w, 693 w cm^{-1}.

NMR: τ 2.42, multiplet, C_6H_5; τ 3.96, doublet *J*(P–H) 0.8 Hz, C_5H_5; τ 7.43, doublet *J*(P–CH) 10.0 Hz, CH_3.

$Mn(CO)_4[P(C_6H_5)_2H]Br$. A solution of this compound (0.433 g, 1.0 mmol) in 50 ml tetrahydrofuran was treated with 0.444 ml 2.25 *M* n-butyllithium. After refluxing for six days (during which time the infrared spectrum of the mixture was monitored) the solvent was removed and the residue chromatographed on alumina. A single yellow band eluted with 1/1 chloroform/hexane. The resulting product was crystallized from chloroform/heptane; it was identified as $Mn_2(CO)_8[P(C_6H_5)_2]_2$ by comparison of its infrared spectrum and m.p. with literature data[20]. Yield 0.27 g, 76%.

$C_5H_5Fe(CO)[P(C_6H_5)_2H]Br$. The reaction of 0.68 g of this complex (1.64 mmol) and 0.60 ml of 2.25 *M* n-butyllithium in tetrahydrofuran was run for 2 h. Work-up, as above, afforded a small amount of *cis*-$[C_5H_5Fe(CO)P(C_6H_5)_2]_2$, identified by its infrared spectrum and m.p.[19]. Yield 0.021 g, 4%.

$C_5H_5Mo(CO)_2[P(C_6H_5)_2H]Br$. The reaction of 1.207 g of this substance with 1.19 ml of 2.11 *M* n-butyllithium in 100 ml of tetrahydrofuran was run for 16 h at 25°.

Workup, involving chromatography on Florisil, gave the orange crystalline product $(C_5H_5Mo)_2(CO)_4[P(C_6H_5)_2]H$. Yield 0.105 g, 13.5%; m.p. 197–201°. (Found: C, 51.3; H, 3.81; P, 4.58; mol. wt., 594. $C_{26}H_{21}Mo_2O_4P$ calcd.: C, 51.4; H, 3.39; P, 5.00%; mol. wt., 620.)

Infrared (in heptane): ν(CO), 1944.5 s, 1881 s cm^{-1}; other bands: 1431 m, 1089 w, 997 w, 808 m, 745 m, 738 m, 715 w, 689 m cm^{-1}.

NMR ($CDCl_3$): τ 2.71, multiplet, C_5H_5; τ 5.10, singlet C_5H_5; the MoHMo proton was not observed due to low solubility.

Irradiation of secondary phosphine complexes and of their metallated derivatives

$W(CO)_5P(C_6H_5)_2H$. A 1.00 g sample of this compound (1.95 mmol) in 200 ml tetrahydrofuran was irradiated with ultraviolet light for 28 h. The solvent was then removed and the residue chromatographed on alumina. Hexane/chloroform (4/1) eluted a light red band. Solvent was evaporated and the residue crystallized from chloroform/heptane to give $W_2(CO)_8[P(C_6H_5)_2]_2$[21]. Yield 0.097 g, 5.1%. A second band eluted with chloroform. Recrystallization of the product from this band with the same solvent mixture gave red crystals of $W_2(CO)_7[P(C_6H_5)_2]_2[P(C_6H_5)_2H]$. Yield 0.36 g, 50%; m.p. 192–194°. (Found: C, 45.9; H, 3.02; P, 8.27; mol. wt., 1000. $C_{43}H_{31}O_7P_3W_2$: C, 46.1; H, 2.77; P, 8.31%; mol. wt., 1120.)

Infrared (in CH_2Cl_2): ν(CO), 2046 m, 2004 m, 1936 vw(br) cm^{-1}, ν(P–H), 2340 vw cm^{-1}; other bands: 1432 m, 1342 w, 1300 vw, 1265 vw, 1180 w, 1155 w, 1088 w, 1065 w, 871 w, 849 w, 840 w, 739 m, 715 w, 690 m cm^{-1}.

NMR ($CDCl_3$): τ 2.30, two 1/1/1/1 quartets, J(P–H) 370 Hz, J(P′–H) 14 Hz, J(P″–H) 2 Hz, PH; τ 2.58, multiplet, C_6H_5 (all).

$Mo(CO)_5P(C_6H_5)_2H$. Irradiation of 200 g (4.74 mmol) of this compound in 200 ml of tetrahydrofuran for 4 days was carried out. Workup, utilizing chromatography as described above yielded 1.05 g starting material (52%) eluting with hexane, and a trace of $Mo(CO)_4[P(C_6H_5)_2H]_2$ eluting with chloroform. The latter was identified by comparison of its infrared spectrum with the spectrum of a known sample[5].

$Cr(CO)_5P(C_6H_5)_2H$. This compound (2.16 g, 5.78 mmol) in 200 ml of tetrahydrofuran was irradiated for 18 h. Chromatography of the products gave 1.02 g starting material (47%) eluting with 9/1 hexane/chloroform. Chloroform eluted a yellow band, which on workup yielded white crystals of *cis*-$Cr(CO)_4[P(C_6H_5)_2H]_2$, recrystallized from dichloromethane/heptane. Yield 0.56 g, 28.6%; m.p. 127–129°. (Found: C, 62.4; H, 4.09; P, 11.2; mol. wt., 491. $C_{28}H_{22}CrO_4P_2$ calcd.: C, 62.6; H, 4.10; P, 11.6%; mol. wt., 536.)

Infrared (in heptane): ν(CO), 2019.5 m, 1930 m, 1911 s, 1902 s cm^{-1}; ν(P–H) 2340 vw cm^{-1}; other bands: 1482 w, 1463 w, 1438 m, 1380 w, 910 w, 885 w, 866 w, 735 w, 718 w, 690 w, 666 w, 643 m cm^{-1}.

NMR ($CDCl_3$): τ 2.54, multiplet, C_6H_5; τ 3.84, doublet J(P–H) 344 Hz, PH.

$W(CO)_5P(C_6H_5)_2Li$. A 2.052 g sample of $W(CO)_5P(C_6H_5)_2H$ (4.04 mmol) was dissolved in 200 ml tetrahydrofuran and reacted with 1.91 ml of 2.11 *M* n-butyllithium. The solution was then irradiated for 24 h. The solvent was removed and the residue crystallized from chloroform/heptane, giving red crystalline $W_2(CO)_8[P(C_6H_5)_2]_2$, identified by comparison of its infrared spectrum and m.p. with literature data[21]. Yield 1.50 g, 77%.

$Mo(CO)_5P(C_6H_5)_2Li$. A 3.00 g sample of $Mo(CO)_5P(C_6H_5)_2H$ (7.10 mmol)

was dissolved in 250 ml tetrahydrofuran and deprotonated with 5.24 ml of 1.355 *M* n-butyllithium. The solution was irradiated for 2 h; then the solvent was removed. The residue was dissolved in 250 ml chloroform, and chromatographed over alumina; the product eluted with chloroform. Heptane was added to the chloroform eluate. Solvent was slowly removed causing the product, $Mo_2(CO)_8[P(C_6H_5)_2]_2$, to precipitate. This material was obtained as orange crystals, 1.40 g, 50.1% yield. It was identified by comparison of its infrared spectrum with the literature spectrum[21].

$Cr(CO)_5P(C_6H_5)_2Li$. $Cr(CO)_5P(C_6H_5)_2Li$, prepared from 3.00 g (7.94 mmol) $Cr(CO)_5P(C_6H_5)_2H$ and 5.24 ml of 1.355 *M* n-butyllithium, was irradiated for 24 h. Chromatography of the reaction product on alumina gave the order of elution: (*a*) starting material, 0.54 g, 18% recovery, eluting with 1/9 $CHCl_3$/hexane, and (*b*) *cis*-$Cr(CO)_4[P(C_6H_5)_2H]_2$, 0.43 g, 27% conversion, eluting with 1/1 $CHCl_3$/hexane.

$Fe(CO)_4P(C_6H_5)_2Li$. Deprotonation of 3.0 g (8.48 mmol) $Fe(CO)_4P(C_6H_5)_2H$ in 250 ml tetrahydrofuran, with 6.26 ml of 1.355 *M* n-butyllithium, followed by irradiation for 25 h, gave one product, $Fe_2(CO)_6[P(C_6H_5)_2]_2$, which was worked up as described above[22]. Yield 0.27 g, 9.9%.

$[C_5H_5Fe(CO)_2\{P(C_6H_5)_2H\}]PF_6$. A solution of $[C_5H_5Fe(CO)_2\{P(C_6H_5)_2H\}]PF_6$ (5.00 g, 9.86 mmol) in 1000 ml tetrahydrofuran was irradiated for 4 h. The solution turned green and then yellow. The solvent was removed and the residue dissolved in chloroform, and chromatographed on alumina. A single yellow band developed which was eluted with acetone. After evaporation of the acetone, the solid was dissolved in 750 ml ethanol and 10.0 g NH_4PF_6 was added. The product was precipitated on addition of 750 ml water. This process was repeated twice more. The solid was then dissolved in 150 ml methanol, and 850 ml of ethyl ether was added. Yellow crystals formed overnight at −20°. The yellow crystalline product, 1.00 g, 19% yield, was identified as $[(C_5H_5Fe)_2\{P_2(C_6H_5)_4\}_2\{P(C_6H_5)_2H\}_2](PF_6)_2$, m.p. 183–184°. (Found: C, 61.3; H, 5.34; P, 15.0. $C_{82}H_{72}F_{12}FeP_8$ calcd.: C, 59.9; H, 4.38; P, 15.1%.)

Infrared: ν(P–H), 2320 w cm^{-1}; other bands: 1588 vw, 1573 w, 1483 m, 1438 s, 1420 m, 1414 m, 1362 vw, 1337 vw, 1314 w, 1296 w, 1188 vw, 1160 w, 1115 vw, 1097 s, 1067 m, 1117 vw, 996 m, 952 vw, 927 vw, 887 s, 863 (sh), 835 vs (PF_6^-), 818 s, 747 m, 740 m, 730 m, 690 s cm^{-1}.

NMR (Varian XL-100 Spectrometer, acetone-d_6): τ 2.35, multiplet, intensity 60, C_6H_5; τ 5.07, 1/3/3/1 quartet, J(P–H) 1.7 Hz, intensity 10, C_5H_5; τ 3.44, doublet, J(P–H) 369 Hz, intensity 2, PH.

RESULTS AND DISCUSSION

The reactions of phenylphosphine and diphenylphosphine with metal carbonyls and their derivatives proceeded with ligand substitution. The following reactions were studied:

1. The reaction of $C_5H_5Fe(CO)_2Br$ with diphenylphosphine (L) gave mixtures of the cationic species $[C_5H_5Fe(CO)_2L]Br$ and the uncharged $C_5H_5Fe(CO)(L)Br$. The reaction of $C_5H_5Fe(CO)_2I$ and phenylphosphine (L′) occurred in an analogous manner. The uncharged species are fairly unstable and were characterized from spectral data. These reactions are analogous to a number of reported reactions of $C_5H_5Fe(CO)_2X$ species with several phosphines[23,24].

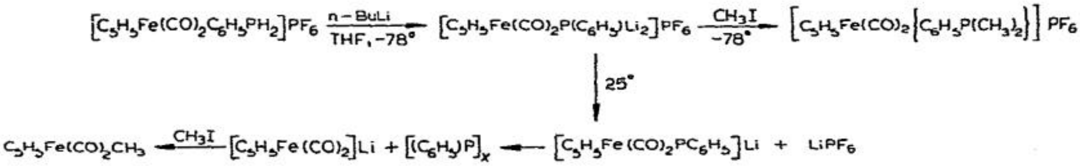
2. The reaction of $C_5H_5Mo(CO)_3Br$ and diphenylphosphine (L) proceeded with carbonyl replacement giving $C_5H_5Mo(CO)_2(L)Br$; but in the presence of aluminum chloride the cationic species $[C_5H_5Mo(CO)_3(L)]AlX_4$ was formed. These are the established reactions for syntheses of complexes of these types[25].
3. Reactions of either phosphine, L or L', with $Mn(CO)_5Br$ or with $Mn_2(CO)_8Br_2$ gave mixtures of two products with either one or two carbonyls replaced by the phosphine; many other complexes analogous to $Mn(CO)_4(L)Br$ and $Mn(CO)_3L_2Br$ are known[6], and are formed in the same way.
4. Phenylmanganese pentacarbonyl and diphenylphosphine react in refluxing ether (18 h), giving $C_6H_5Mn(CO)_4(L)$ in small yield. Presumably this reaction has occurred via an acyl complex which has undergone decarbonylation[26], as this is the general reaction mechanism observed in all previous instances.
5. Reactions of phenylphosphine (L') with $Cr(CO)_3(NCCH_3)_3$ and with (norbornadiene)$Mo(CO)_4$ gave *cis*-$Cr(CO)_4L'_2$ and *fac*-$Mo(CO)_3L'_3$ respectively. The chromium tetracarbonyl complex formation from $Cr(CO)_3(NCCH_3)_3$ involves ligand redistribution, with an additional carbon monoxide probably arising from decomposition. The yield of this complex was very small, and no other metal complexes were seen. Even using fairly mild conditions the favored product of the (norbornadiene)$Mo(CO)_4$ reaction was $Mo(CO)_3L_3$. Again the yield was quite small.

The new complexes described here have received appropriate characterization by elemental analyses, and by infrared and NMR spectroscopy.

We are interested in the reactivities of coordinated ligands, and the P–H functionality in metal complexes of primary and secondary phosphines seems an ideal subject for this study. Two reactions, deprotonation and loss of hydrogen (unspecified) to give phosphido complexes, were observed in our earlier work[9,10]; a study of these reactions has been expanded here.

We have described deprotonation reactions of the metal complexes $Fe_2(CO)_6(C_6H_5PH)_2$, $Fe(CO)_4P(C_6H_5)(CH_3)H$, $Fe(CO)_4L$, $C_5H_4CH_3Mn(CO)_2L$, and $M(CO)_5L$ $[L=P(C_6H_5)_2H, M=Cr, Mo, W]$, using an appropriate base such as n-butyllithium. Deprotonation followed by addition of methyl iodide gave the appropriate phenylmethylphosphine complexes in good yield[10]. Analogous reactions were carried out here with the cationic complexes. $[C_5H_5Fe(CO)_2L]PF_6$ and $[C_5H_5Mo(CO)_3L]PF_6$ $[L=P(C_6H_5)_2H]$. These complexes were sufficiently protonic to react with methoxide ion to give $C_5H_5Fe(CO)_2P(C_6H_5)_2$ and $C_5H_5Mo(CO)_3P(C_6H_5)_2$. As expected each reacts readily with methyl iodide to give the cationic diphenylmethylphosphine complexes $[C_5H_5Fe(CO)_2\{P(C_6H_5)_2CH_3\}]PF_6$ and $[C_6H_5Mo(CO)_3\{P(C_6H_5)_2CH_3\}]PF_6$. These alkylations are quite reasonable in view of the considerable basicity expected for the intermediate complexes[27].

The deprotonation reaction of $[C_5H_5Fe(CO)_2C_6H_5PH_2]PF_6$ was rather interesting. Using n-butyllithium at −78° both protons on the coordinated phosphine could be removed. If the reaction product was allowed to warm from −78° in the presence of methyl iodide, only the alkylated product $[C_5H_5Fe(CO)_2\{C_6H_5P(CH_3)_2\}]PF_6$ was obtained. If, however, the solution was formed initially at −78°, and then was warmed to 25°, and methyl iodide was subsequently added, $C_5H_5Fe(CO)_2CH_3$ was obtained instead. Presumably the intermediate $[C_5H_5Fe(CO)_2P(C_6H_5)Li_2]PF_6$ is unstable, degrading via $[C_5H_5Fe(CO)_2P(C_6H_5)]Li$ to $[C_5H_5Fe(CO)_2]Li$ which reacts as expected with methyl iodide[14].



Although there are no previous data to cite, it seems reasonable that this decomposition reaction of $[C_5H_5Fe(CO)_2(PC_6H_5)]Li$ would proceed in this fashion. Neither $(PC_6H_5)_x$ (nor S_8) are reported to react with the anion $C_5H_5Fe(CO)_2^-$.

A number of other reactions were studied which involved initial deprotonation of a metal complex and the subsequent reaction or rearrangement of the deprotonated species. The phosphine-substituted metal carbonyl halides provided an interesting group of complexes for study. A reasonable expectation was that the deprotonated species would undergo halide loss and dimerization. Indeed this occurred with both $Mn(CO)_4[P(C_6H_5)_2H]Br$ and $C_5H_5Fe(CO)[P(C_6H_5)_2H]Br$, although in the latter reaction the yield of $[C_5H_5Fe(CO)P(C_6H_5)_2]_2$[19] was quite poor. Interestingly, the reaction rate for the loss of Br^- from $[Mn(CO)_4(PR_2)Li]Br$ was slow. The reaction, which was monitored by infrared spectroscopy, took 6 days to reach completion; the resulting product, $[Mn(CO)_4P(C_6H_5)_2]_2$, a known complex[20], was obtained in 76% yield.

$$Mn(CO)_4[P(C_6H_5)_2H]Br \xrightarrow[\text{THF}]{\text{n-BuLi}} Mn(CO)_4[P(C_6H_5)_2Li]Br$$
$$\xrightarrow[\text{6 days}]{-\text{LiBr}} [Mn(CO)_4P(C_6H_5)_2]_2$$

$$C_5H_5Fe(CO)[P(C_6H_5)_2H]Br \xrightarrow[\text{THF}]{\text{n-BuLi}} C_5H_5Fe(CO)[P(C_6H_5)_2Li]Br$$
$$\xrightarrow[\text{2 h}]{-\text{LiBr}} [C_5H_5Fe(CO)P(C_6H_5)_2]_2$$

The complex $C_5H_5Mo(CO)_2[P(C_6H_5)_2H]Br$, after deprotonation, reacted in a different fashion giving the hydride bridged species $(C_5H_5Mo)_2(CO)_4[P(C_6H_5)_2]H$; an analogous complex with a bridging dimethylphosphido group is known[28].

Because of the basicity of a $-PR_2$ group bonded to a metal, one would expect complexes containing this group to dimerize readily. The analogous reaction with metal–SR complexes is already well documented[8], the dimerization tendency being inversely related to the electron-withdrawing power of the groups bonded to the sulfur. Of course, the deprotonation reaction generates a phosphido complex so it is appropriate to observe whether the dimerization reaction will occur either thermally or photolytically. At the same time, it should be pointed out that the secondary phosphine iron tetracarbonyl complexes may also dimerize with hydrogen loss on irradiation. We observed earlier[9] that both $Fe(CO)_4[P(C_6H_5)_2H]$ and $Fe(CO)_4[P(CH_3)_2H]$ give the appropriate $Fe_2(CO)_6(PR_2)_2$ complex in good yield upon irradiation.

When the cationic species $[C_5H_5Fe(CO)_2P(C_6H_5)_2H]PF_6$ was deprotonated the resulting phosphido complex obtained was quite stable. However, in refluxing tetrahydrofuran (36 h), it slowly dimerized to a mixture of known *cis*- and *trans*-$[C_5H_5Fe(CO)P(C_6H_5)_2]_2$[19]. The partial deprotonation of $[C_5H_5Fe(CO)_2C_6H_5PH_2]PF_6$ at room temperature, controlled by the amount of alkyllithium added, was accompanied by rapid carbon monoxide evolution; the red, dimeric product $[C_5H_5Fe(CO)C_6H_5PH]_2$ was obtained as a mixture of isomers. Deprotonation of $[C_5H_5Mo(CO)_3P(C_6H_5)_2H]PF_6$ led only to decomposition. The failure to obtain a dinuclear complex, $[C_5H_5Mo(CO)_2P(C_6H_5)_2]_2$, is noteworthy; Hayter was unable to make this complex by the standard route from $[C_5H_5Mo(CO)_3]_2$ and $P_2(C_6H_5)_4$[28].

It is interesting to compare the thermal dimerization of $C_5H_5Fe(CO)_2P(C_6H_5)_2$ with the reaction of $[C_5H_5Fe(CO)_2P(C_6H_5)_2H]PF_6$ upon ultraviolet irradiation. The yellow reaction mixture rapidly turned green and then became yellow again. Workup of the reaction mixture gave a compound which was an electrolyte, and which contained the hexafluorophosphate anion, according to the infrared spectrum. In addition, the complex contained P–H groups but no carbonyl groups. The NMR spectrum showed phenyl, cyclopentadienyl, and PH protons, in the ratio 60/10/2. The molecular weight in chloroform (osmometric) was observed over a concentration range to vary from about 1700 (high concentration; one assumes little ionization) to about 650 (extrapolation to zero concentration, where one may assume complete ionization and expect a value equal to $M/3$). These data, with accompanying elemental analyses and NMR spectrum suggest the formulation $[(C_5H_5Fe)_2\{P_2(C_6H_5)_4\}_2\{P(C_6H_5)_2H\}_2](PF_6)_2$, for which the structure (I), Fig. 1, may be suggested.

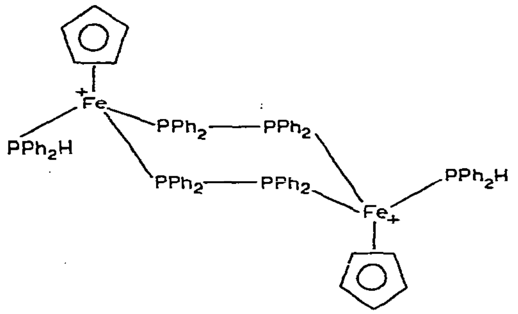


Fig. 1. Proposed structure of the $[C_5H_5Fe)_2\{P_2(C_6H_5)_4\}_2\{P(C_6H_5)_2H\}_2]$ dictation.

Finally, we carried out the irradiations of $M(CO)_5[P(C_6H_5)_2H]$ and $[M(CO)_5P(C_6H_5)_2]Li$ (M=Cr, Mo, W). The results of these reactions are given in Table 1.

In all the reactions some decomposition was noted. It was generally possible to follow the reaction progress, however, by monitoring the decreasing intensities of $\nu(CO)$ for the starting material.

A few comments on these data are in order. It is clear that there is no general reaction observed here although dimerization to complexes with bridging phosphido groups seems to predominate. The dimerization of the anionic phosphido complexes is accompanied by oxidation, perhaps by the solvent. The reaction below can be postulated:

$$[M(CO)_5PR_2Li] \rightarrow [M_2(CO)_8(PR_2)_2]Li \xrightarrow{\text{oxid.}} M_2(CO)_8(PR_2)_2$$

Analogous intermediate dianion species ($R{=}CH_3$) were previously known, having been observed in electrochemical reductions of the $M_2(CO)_8(PR_2)_2$[29]. They have not been isolated however, presumably due to their susceptibility to oxidation.

TABLE I

IRRADIATIONS OF $M(CO)_nPR_2H$ and $[M(CO)_nPR_2]Li$

Cr, Mo, W, $n=5$; Fe, $n=4$

Reactant[a]	*Time*	*Product(s), (Yield)*
$Cr(CO)_5PR_2H$	18 h	Starting material (47%), *cis*-$Cr(CO)_4(PR_2H)_2$ (29%)
$Mo(CO)_5PR_2H$	4 days	Starting material (52%), *cis*-$Mo(CO)_4(PR_2H)_2$ (tr)
$W(CO)_5PR_2H$	28 h	$W_2(CO)_8(PR_2)_2$ (5%), $W_2(CO)_7(PR_2)_2PR_2H$ (50%)
$Fe(CO)_4PR_2H$	24 h	$Fe_2(CO)_6(PR_2)_2$ (81%)
$[Cr(CO)_5PR_2]Li$	24 h	Starting material (18%), *cis*-$Cr(CO)_4(PR_2H)_2$ (27%)
$[Mo(CO)_5PR_2]Li$	2 h	$Mo_2(CO)_8(PR_2)_2$ (50%)
$[W(CO)_5PR_2]Li$	24 h	$W_2(CO)_8(PR_2)_2$ (77%)
$[Fe(CO)_4PR_2]Li$	25 h	$Fe_2(CO)_6(PR_2)_2$ (10%)

[a] $R=C_6H_5$

The main alternative to dimerization would appear to be a ligand redistribution, particularly in the case of the chromium complexes where this is the only reaction observed. It is interesting to note that ligand redistribution takes place for $Mo(CO)_5PR_2H$, whereas dimerization occurs for the deprotonated complex. This is reasonable in that for deprotonated species the high negative charge would lead to stronger π bonding to the ligands (in particular to the phosphido group) and hence a stronger metal–ligand bond.

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