description of the proton contact shifts will be very difficult to achieve. If the model used for interpretation of the magnetic susceptibilities is correct, the temperature dependence of contact shifts will be difficult to assess, especially near room temperature where the relative population of low-energy electronic levels may be changing rapidly. It probably is fortuitous that the proton contact shifts reported by Butcher, *et al.*,[3] and magnetic susceptibilities reported by the same authors show a T^{-1} or $(T + \Theta)^{-1}$ temperature dependence.

Registry No. $WCl_4[S(C_2H_5)_2]_2$, 40354-86-7; $WCl_4(SC_4H_8)_2$, 40354-87-8; $WCl_4(CH_3CN)_2$, 40354-88-9; $WCl_4(C_2H_5CN)_2$, 40354-89-0; $WCl_4(C_3H_7CN)_2$, 40354-90-3; $WBr_4(CH_3CN)_2$, 40354-91-4; $WBr_4(C_3H_7CN)_2$, 12081-02-6; $WCl_4[P(C_6H_5)_3]_2$, 36151-25-4; WCl_4, 13470-13-8; WCl_5, 13470-14-9; WBr_4, 14055-81-3.

Contribution from the Department of Chemistry,
Memphis State University, Memphis, Tennessee 38152

Transition Metal π Complexes. II. Reactions of π-Cycloheptatrienylmolybdenum Dicarbonyl Iodide with Chelating Group Va Ligands[1]

THOMAS W. BEALL and LARRY W. HOUK*

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Reactions of π-cycloheptatrienylmolybdenum dicarbonyl iodide (I) with several potentially bidentate group Va ligands have led to the formation of five types of derivatives: h^7-C_7H_7MoCO(ligand)I, h^3-$C_7H_7Mo(CO)_2$(ligand)I, $[h^7$-$C_7H_7Mo(CO)_2$(ligand)$]^+PF_6^-$, $[h^7$-C_7H_7MoCO(ligand)$]^+PF_6^-$, and h^7-C_7H_7Mo(ligand)I. The interaction of the tritertiary chelating agent $CH_3C[CH_2P(C_6H_5)_2]_3$ (triphos) with $C_7H_7Mo(CO)_2I$ resulted in the isolation of the nonsaline C_7H_7MoCO(triphos)I and the ionic $[C_7H_7Mo(\text{triphos})]^+I^-$. Formulas and structures of the new complexes were ascertained from infrared and nmr spectral data.

Introduction

In contrast to the numerous accounts of π-cyclopentadienylmetal carbonyl reactions with group Va tertiary and oligotertiary ligands that have been reported in the past 20 years,[2] the analogous chemistry of other π-bonded ring metal carbonyls has been much less studied. Moreover, although a few tertiary phosphine and phosphite complexes are contained in two previous papers,[1,3] no reports have appeared describing reactions of π-cycloheptatrienyl group VIb metal carbonyls with chelating Lewis base ligands.

In a modest attempt to fill this void and to contrast π-cyclopentadienyl- and π-cycloheptatrienylmetal carbonyl chemistry, we have investigated reactions of π-cycloheptatrienylmolybdenum dicarbonyl iodide with one group Va tridentate ligand and a variety of bidentate ligands.

Experimental Section

Microanalyses and molecular weights were performed by M-H-W Laboratory, Garden City, Mich. Infrared spectra were recorded in methylene chloride solutions and KBr pellets on a Model 621 Perkin-Elmer spectrometer. Proton nmr spectra were taken on Varian Associates Model T-60 and HA-100 machines in chloroform-*d* and acetone-d_6 with tetramethylsilane and hexamethyldisiloxane as internal standards, respectively. Conductivity measurements were made on 10^{-3} *M* nitrobenzene solutions using an Industrial Instruments conductivity bridge, Model RC 16B2, and a cell with platinum electrodes. Melting points were taken in open capillaries and are uncorrected. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels.

Reagents. The ligands 1,2-bis(diphenylphosphino)ethane[4] (diphos), *cis*-1,2-bis(diphenylphosphino)ethylene[5] (*cis*-diphos), 1,2-bis(dimethylphosphino)ethane[6] (mdiphos), bis(diphenylstibino)methane[7] (distib), 2-(2-diphenylphosphinoethyl)pyridine[8] (pyphos), and 1,1,1-tris(diphenylphosphinomethyl)ethane[9] (triphos) were synthesized according to literature procedures. Chemicals obtained commercially were bis(diphenylarsino)methane (arsars) (Strem Chemicals, Inc., Danvers, Mass.), 1-diphenylphosphino-2-diphenylarsinoethane (phosars) (Pressure Chem. Co., Pittsburgh, Pa.), 2-vinylpyridine (Reilly Tar and Chemical Corp., New York, N. Y.), triphenylphosphine and triphenylstibine (M and T Chemical Co., Inc., Rahway, N. J.), α,α′-dipyridyl (Aldrich Chemical Co., Inc., Milwaukee, Wis.), and Florisil (60–100 mesh) used for column chromatography and *o*-phenanthroline (Fisher Scientific Co., Fair Lawn, N. J.). The metal carbonyl precursor $C_7H_7Mo(CO)_2I$ was prepared by a literature method.[10]

Syntheses. The basic synthetic procedure involved stirring equimolar amounts of $C_7H_7Mo(CO)_2I$ and ligand in benzene at either ambient or reflux temperatures. Lengths of the reaction periods (Table I) were determined by monitoring the ν(CO) stretching frequencies in the infrared spectra. Filtration and/or evaporation of the solvent resulted in solid residues which were purified by recrystallization from CH_2Cl_2–hexane mixtures. Iodide salts were converted to hexafluorophosphates by dissolution in acetone followed by the addition of NH_4PF_6 in water and the slow evaporation of acetone. The precipitated solid then was recrystallized from acetone–benzene. A few typical preparations are as follows.

$C_7H_7Mo(CO)_2$(diphos)I. Equimolar quantities of $C_7H_7Mo(CO)_2I$ and diphos were stirred at 25° in benzene for 24 hr. The solvent was evaporated (25°, 40 mm) and the product was recrystallized from CH_2Cl_2–hexane.

$[C_7H_7Mo(CO)_2$(diphos)$]^+PF_6^-$. $C_7H_7Mo(CO)_2$(diphos)I (0.4 g) was dissolved in acetone (100 ml) and NH_4PF_6 (2 g) in water (100 ml) was added. After 2 hr of stirring at 25° the acetone was evaporated (25°, 40 mm), the solid was collected and redissolved in acetone, and NH_4PF_6 (2 g) in water was added. After two further

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[1] Part I: T. W. Beall and L. W. Houk, *Inorg. Chem.*, 11, 915 (1972).

[2] Some references in addition to those in ref 1 include: R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, 7, 2353 (1968); R. B. King, L. W. Houk, and P. N. Kapoor, *ibid.*, 8, 1792 (1969); R. B. King, L. W. Houk, and K. H. Pannell, *ibid.*, 8, 1042 (1969); K. W. Barnett and D. W. Slocum, *J. Organometal. Chem.*, 44, 1 (1972).

[3] R. B. King, *Inorg. Chem.*, 2, 936 (1963).

[4] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[5] A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, 86, 2299 (1964).

[6] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961).

[7] Y. Matsumura and R. Okawara, *J. Organometal. Chem.*, 25, 439 (1970).

[8] V. E. Uhlig and M. Maaser, *Z. Anorg. Allg. Chem.*, 344, 205 (1966).

[9] R. B. King, L. W. Houk, and K. H. Pannell, *Inorg. Chem.*, 8, 1042 (1969).

[10] D. J. Bertelli, Ph.D. Thesis, University of Washington, 1961.

treatments with NH_4PF_6, the residue was stirred with benzene to remove traces of $C_7H_7Mo(CO)_2$(diphos)I and then recrystallized from acetone-benzene.

$[C_7H_7MoCO(diphos)]^+PF_6^-$. $C_7H_7Mo(CO)_2I$ and diphos in equimolar amounts were stirred in benzene at 80° for 15 hr. After filtration the solid was dissolved in acetone, treated with NH_4PF_6 in water, and stirred at 25° for 2 hr. After the NH_4PF_6 procedure was repeated, the product was collected and recrystallized from acetone-benzene.

C_7H_7Mo(diphos)I. The filtrate from the previous preparation was evaporated (25°, 40 mm) and the residue was recrystallized from CH_2Cl_2-hexane.

Infrared Spectra (cm^{-1}) (KBr Pellets). (A) $C_7H_7Mo(CO)_2$-$(C_6H_5)_2PC_2H_4P(C_6H_5)_2I$: 3049 (w), 3017 (w), 2914 (w), ν(CO) bands in Table II, 1583 (w), 1568 (w), 1539 (w), 1481 (w), 1431 (s), 1409 (m), 1381 (m), 1304 (w), 1186 (w), 1155 (w), 1092 (s), 1019 (w), 1023 (w), 998 (w), 886 (m), 813 (m), 741 (s), 704 (sh), 694 (s), 670 (w), 647 (w), 554 (w), 514 (m). **(B) $[C_7H_7Mo(CO)_2(C_6H_5)_2$-$PC_2H_4P(C_6H_5)_2]^+PF_6^-$:** 3076 (sh), 3035 (m, br), 2990 (sh), ν(CO) bands in Table II, 1586 (m), 1578 (sh), 1481 (s), 1461 (sh), 1443 (sh), 1435 (s), 1425 (sh), 1329 (sh), 1307 (m), 1258 (m), 1166 (s), 1093 (s), 1073 (sh), 1028 (m), 1000 (m), 969 (sh), 915 (sh), 808 (vs), 740 (s), 727 (s), 689 (vs), 609 (sh), 550 (vs), 509 (vs). **(C) $[C_7H_7MoCO(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+PF_6^-$:** 3054 (m), 2926 (w), ν(CO) band in Table II, 1583 (w), 1569 (w), 1482 (m), 1433 (s), 1414 (w), 1382 (w), 1309 (w), 1185 (w), 1196 (s), 1035 (w), 997 (m), 871 (sh), 843 (s), 814 (sh), 748 (s), 696 (s), 674 (m), 651 (w), 556 (s), 524 (s). **(D) $C_7H_7Mo(C_6H_5)_2PC_2H_4P(C_6H_5)_2I$:** 3068 (m), 3038 (s), 2983 (w), 2961 (w), 2918 (m), 1582 (m), 1480 (s), 1431 (s), 1381 (m), 1304 (m), 1260 (s), 1185 (m), 1157 (w), 1094 (s), 1070 (m), 1025 (s), 997 (m), 961 (m), 865 (m), 845 (w), 813 (s), 805 (sh), 785 (sh), 742 (s), 694 (s), 656 (m), 520 (s), 510 (sh). **(E) $[C_7H_7MoCO(CH_3)_2PC_2H_4P(CH_3)_2]^+PF_6^-$:** 3079 (w), 2979 (w), 2907 (w), ν(CO) band in Table II, 1612 (w), 1479 (w), 1426 (s), 1381 (w), 1307 (m), 1290 (s), 1246 (w), 1137 (w), 1085 (w), 995 (w), 950 (s), 935 (s), 901 (m), 874 (sh), 835 (s), 809 (s), 739 (m), 712 (s), 652 (m), 558 (s). **(F) $[C_7H_7Mo((C_6H_5)_2PCH_2)_3CCH_3]^+PF_6^-$:** 3050 (m), 2947 (m), 2920 (m), 1584 (w), 1569 (w), 1481 (s), 1432 (s), 1404 (w), 1382 (w), 1307 (w), 1270 (w), 1221 (w), 1186 (m), 1157 (w), 1085 (s), 1025 (w), 999 (m), 867 (sh), 834 (s), 813 (sh), 740 (s), 722 (m), 697 (s), 558 (s), 509 (s). **(G) $C_7H_7MoCOC_5H_4NC_2H_4P(C_6H_5)_2$:** 3078 (sh), 3050 (m), 2951 (w), 2914 (w), ν(CO) band in Table II, 1605 (s), 1569 (sh), 1479 (s), 1439 (sh), 1435 (s), 1409 (sh), 1338 (sh), 1314 (m), 1264 (m), 1247 (m), 1190 (sh), 1161 (m), 1141 (sh), 1099 (s), 1070 (m), 1025 (w), 998 (m), 965 (w), 947 (sh), 919 (m), 814 (vs), 768 (s), 752 (sh), 748 (s), 699 (s), 677 (s), 645 (w), 559 (s), 528 (s), 511 (s), 479 (s), 424 (sh), 410 (m). **(H) $C_7H_7MoC_{12}H_8N_2I$:** (ν(CH) too weak to assign) 1544 (w), 1492 (m), 1440 (sh), 1418 (s), 1407 (s), 1335 (sh), 1262 (s), 1238 (sh), 1221 (sh), 1207 (sh), 1186 (s), 1168 (sh), 1128 (s), 1090 (s), 1047 (s), 1038 (sh), 960 (m), 914 (w), 888 (w), 876 (w), 833 (s), 811 (s), 773 (s), 729 (s), 708 (s), 634 (w). **(I) $C_7H_7MoCO(C_6H_5)_2SbCH_2Sb(C_6H_5)_2I$:** 3066 (sh), 3040 (m, br), 3015 (sh), ν(CO) band in Table II, 1572 (m), 1476 (m), 1428 (s), 1374 (sh), 1340 (sh), 1327 (w), 1295 (w), 1260 (w), 1242 (w), 1178 (sh), 1155 (w), 1066 (s), 1019 (m), 998 (m), 958 (m), 905 (w), 867 (sh), 855 (m), 810 (s), 730 (vs), 698 (s), 658 (w), 635 (m), 535 (w), 495 (w), 447 (w).

Results and Discussion

Cycloheptatrienylmolybdenum dicarbonyl iodide (I) reacted with a variety of group Va bidentate ligands to yield five different types of derivatives. Structures of these compounds were established based upon infrared spectra of the metal-carbonyl stretching region and nmr data along with elemental analyses and conductivity measurements. Even though a wide diversity in behavior of I with the studied ligands was manifested, Figure 1 adequately describes the overall reaction sequence and partition of the resulting complexes.

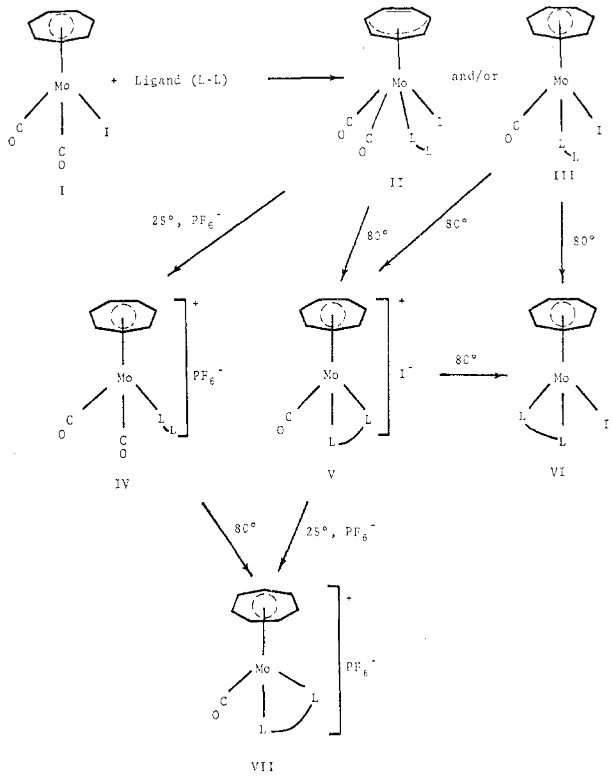

Figure 1.

Although syntheses were conducted routinely at ambient and reflux temperatures, an initial division of products and pathways was evident as the various bidentate chelating agents were allowed to react with I. For those reactions that proceeded at 25° (I with 1,2-bis(diphenylphosphino)ethane (diphos), *cis*-1,2-bis(diphenylphosphino)ethylene (*cis*-diphos), and 1-diphenylphosphino-2-diphenylarsinoethane (phosars)) the isolated dicarbonyl derivatives (II) contained the ligand functioning as a bidentate and the cycloheptatrienyl ring exhibiting a trihapto configuration.[11] As benzene solutions of these compounds were refluxed, the iodine atom became ionic, 1 mol of carbon monoxide was evolved, and the trihapto configuration became heptahapto resulting in derivatives with the structure shown in V. Metathesis with NH_4PF_6 in acetone-water easily exchanged anions (V → VII). Due to limited solubility in benzene, a demonstration of the convertibility of V to VI was conducted in dichloroethane-benzene. The latter derivatives were characterized by their lack of ν(CO) in the infrared spectra as well as elemental analyses and low conductivities in nitrobenzene. Through displacement of the iodine atom as an iodide ion and conversion from a trihapto to a heptahapto configuration, the diphos and phosars compounds (II) converted with difficulty upon several treatments at 25° with NH_4PF_6 in acetone-water solutions to complexes adopting structure IV. These could be smoothly converted to VII by refluxing in dichloroethane for 8 hr. In contrast to the behavior of the diphos and phosars complexes (II), the analogous *cis*-diphos derivative easily converted to VII without detection of IV.

Combinations of three products (V, VI, III) resulted from those interactions with I requiring initiation temperatures above 25°. diphos and phosars yielded V and VI which were easily separated due to the low solubility of V in the benzene solvent. Bis(diphenylstibino)methane (distib) and 2-(2-diphenylphosphinoethyl)pyridine (pyphos) produced only the monocarbonyl nonionic derivatives (III); however, further divisive behavior was exhibited with extended 80° reaction conditions when the pyphos and distib complexes converted

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[11] The authors are indebted to a referee for proposing the trihapto configuration for these derivatives and for pointing up the similarity between $C_7H_7Mo(CO)_2I$ reactions with bidentate di(tertiary phosphines) and those with the two double bonds in sodium cyclopentadienide: R. B. King and M. B. Bisnette, *Tetrahedron Lett.*, 1137 (1963).

Table I. Analytical Data and Physical Properties of Cycloheptatrienylmolybdenum Carbonyl Derivatives

Compd	Color	Mp, °C	Reaction time, hr	% yield	Molar cond[a]	Anal. calcd (found), %			
						C	H	P	Other
$C_7H_7Mo(CO)_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2I$[b]	Red	119–121 dec	24	91	2.37	54.71 (54.66)	4.07 (4.26)	8.06 (7.07)	12.49 (12.84) (Mo)
$C_7H_7Mo(CO)_2(C_6H_5)_2PCH{=}CHP(C_6H_5)_2I\cdot C_6H_6$	Red-brown	204–206 dec	144	53	3.46	58.31 (58.15)	4.18 (3.98)	7.34 (7.46)	
$C_7H_7Mo(CO)_2(CH_3)_2PC_2H_4P(CH_3)_2I$	Red	141–144	15	4	1.38	34.64 (34.50)	4.40 (4.39)	11.91 (12.04)	24.40 (24.31) (I)
$[C_7H_7Mo(CO)_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+PF_6^-$	Red	142–145	24	50	27.4	53.45 (53.72)	3.97 (4.21)	11.81 (11.57)	
$[C_7H_7Mo(CO)_2(C_6H_5)_2PC_2H_4As(C_6H_5)_2]^+PF_6^-$	Red	177–178 dec	44	14	28.6	50.62 (50.59)	3.76 (3.83)		11.55 (11.25) (Mo)
$[C_7H_7MoCO(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+PF_6^-$	Red-brown	217–219	15	30	26.0	53.84 (54.44)	4.12 (4.06)	12.25 (12.38)	
$[C_7H_7MoCO(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]^+PF_6^-$	Wine	249–252 dec	1	37	27.6	53.98 (53.56)	3.87 (4.00)	12.28 (12.18)	
$[C_7H_7MoCO(C_6H_5)_2PC_2H_4As(C_6H_5)_2]^+PF_6^-$	Red	237–239 dec	2	52	31.0	50.89 (50.70)	3.89 (3.61)		11.96 (12.13) (Mo)
$[C_7H_7MoCO(CH_3)_2PC_2H_4P(CH_3)_2]^+PF_6^-$	Yellow-green	248–249	15	35	29.0	32.96 (32.91)	4.54 (4.54)	18.21 (17.39)	22.35 (22.48) (F)
$C_7H_7MoCOC_5H_4NC_2H_4P(C_6H_5)_2I$	Green	78–79 dec	5	19	16.4	51.20 (51.39)	3.98 (4.21)	4.86 (4.83)	2.21 (2.24) (N)
$[C_7H_7MoCOC_5H_4NC_2H_4P(C_6H_5)_2]^+PF_6^-$	Green	174–176	5.5	45	28.8	49.78 (49.58)	3.87 (4.05)	9.51 (9.65)	2.15 (1.93) (N)
$C_7H_7MoCO(C_6H_5)_2SbCH_2Sb(C_6H_5)_2I$[c]	Green	145–147 dec	35	12	7.80	43.65 (43.61)	3.22 (3.22)		26.82 (27.06) (Sb)
$C_7H_7MoCOCH_3C[CH_2P(C_6H_5)_2]_3I$	Green	120–122	3	18	24.2	60.88 (61.23)	4.80 (4.85)	9.61 (9.38)	
$[C_7H_7MoCH_3C[CH_2P(C_6H_5)_2]_3]^+I^-\cdot CH_2Cl_2$	Red-purple	217–218 dec	96	55	30.1	57.50 (57.19)	4.72 (4.84)	9.08 (9.22)	
$[C_7H_7MoCH_3C[CH_2P(C_6H_5)_2]_3]^+PF_6^-$	Light purple	210–211 dec	96	19	26.2	60.26 (60.48)	4.82 (4.93)	12.95 (12.92)	11.92 (12.02) (F)
$C_7H_7Mo(C_6H_5)_2PC_2H_4P(C_6H_5)_2I$	Green	192–210 dec	15	23	5.10	55.64 (55.66)	4.39 (4.36)	8.70 (8.85)	
$C_7H_7Mo(C_6H_5)_2PC_2H_4As(C_6H_5)_2I$[d]	Green	150–153 dec	2	32	7.30	52.40 (51.30)	4.13 (4.16)		12.69 (13.19) (Mo)
$C_7H_7Mo(C_6H_5)_2AsCH_2As(C_6H_5)_2I$	Green	150–152 dec	13	23	3.24	48.88 (49.00)	3.72 (3.86)		19.06 (19.13) (As)
$C_7H_7MoC_{12}H_8N_2I$	Green	254–255 dec	4	72	6.13	46.18 (46.68)	3.06 (3.28)		5.67 (6.04) (N)
$C_7H_7MoC_{10}H_8N_2I$	Purple	280–281 dec	6	72	8.74	43.43 (43.08)	3.22 (3.12)		5.96 (5.80) (N)

[a] Conductance ($cm^2\ ohm^{-1}\ mol^{-1}$) of 10^{-3} *M* solutions in nitrobenzene at 27°. Conductance values in the range 22–30 $cm^2\ ohm^{-1}\ mol^{-1}$ have been reported for 1:1 electrolytes: L. W. Houk and G. R. Dobson, *J. Chem. Soc. A*, 1846 (1968); C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956); J. Chatt, F. A. Hart, and H. R. Watson, *ibid.*, 2537 (1962). [b] Mol wt: calcd, 768; found, 770. [c] Mol wt: calcd, 908; found, 940. [d] Mol. wt: calcd, 756; found, 740.

to V and VI, respectively. The bidentate arsine bis(diphenylarsino)methane (arsars) and the bidentate amines *o*-phenanthroline (phen) and α,α′-dipyridyl (dipy) yielded only VI. The latter results are in contrast to $C_5H_5Mo(CO)_3I$ reactions with dipy or phen which produced only ionic derivatives of the type $[C_5H_5Mo(CO)_2(\text{ligand})]^+I^-$.[12] Compounds with structure III are probably formed as labile intermediates for those reactions leading to VI. *cis*-diphos and 1,2-bis(dimethylphosphino)ethane (mdiphos) also resulted in only one product (V).

It is well known that in metal carbonyl derivatives the formal charge on the central metal atom in an isoelectronic series and the overall bonding ability of noncarbonyl ligands have a marked effect on the terminal metal–carbonyl stretching frequencies. As an attempt is made to assign structures for derivatives discussed herein based upon a comparison of ν(CO) stretching frequencies with "model" compounds, the question becomes apparent as to the effectiveness of the cycloheptatrienyl as compared to the cyclopentadienyl ring in removing charge from the metal. To the extent that ν(CO) stretching frequencies reflect the cumulative bonding effect of noncarbonyl groups the ν(CO) values for h^7-$C_7H_7Mo(CO)_2I$ (2031, 1986 cm^{-1}) and h^5-$C_5H_5Ru(CO)_2I$ (2055, 2007 cm^{-1})[13] indicate the *heptahapto*cycloheptatrienyl ring is only slightly less effective than the *pentahapto*cyclopentadienyl ring. Furthermore, the ν(CO) frequencies for h^5-$C_7H_7Fe(CO)_3^+$ (2120, 2070 cm^{-1})[14] and h^5-$C_5H_5Fe(CO)_3^+$ (2150, 2090 cm^{-1})[15] seem to imply an increased bonding ability in the *pentahapto*cyclopentadienyl molecule which is probably due to a resonance effect.

Based upon a comparison of their ν(CO) stretching frequencies (1940, 1860 cm^{-1}) with those of π-$C_3H_5Mo(CO)_2$(diphos)Cl (1937, 1841 cm^{-1}),[16] derivatives of the type $C_7H_7Mo(CO)_2(\text{ligand})I$ (ligand = diphos, *cis*-diphos, mdiphos) were assigned to the trihapto nonsaline structure II. Corrobative evidence was derived from their monomeric molecular weights, low conductivities in nitrobenzene (Table I), and increased solubilities over ionic compounds in benzene. The $\tau(C_7H_7)$ resonance was a triplet (*J* = 1.1 cps) for the mdiphos compound and a broad unresolved band for the diphos and *cis*-diphos complexes. Although decreased solubility precluded temperature measurements low enough

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(12) P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal. Chem.*, 7, 449 (1967).

(13) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

(14) J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Amer. Chem. Soc.*, **86**, 3589 (1964).

(15) R. B. King, *Inorg. Chem.*, 1, 964 (1962).

(16) H. T. Dieck and H. Friedel, *J. Organometal. Chem.*, 14, 375 (1968).

Table II. Infrared and Proton Nmr Spectra of Cycloheptatrienylmolybdenum Carbonyl Derivatives

Compd	ν(CO),[a] cm^{-1}	Solvent[c]	Chem shift data[b]			
			$\tau(C_7H_7)$	$\tau(C_6H_5)$[d]	$\tau(CH_2)$	τ(other)
$C_7H_7Mo(CO)_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2I$	1936 1857	C	4.47 br	2.58	7.70 br	
$C_7H_7Mo(CO)_2(C_6H_5)_2PCH{=}CHP(C_6H_5)_2I\cdot C_6H_6$	1943 1867	C	4.47 br	2.57[e]		~2.57 (CH)
$C_7H_7Mo(CO)_2(CH_3)_2PC_2H_4P(CH_3)_2I$	1938 1848	C	4.50 t (1.1)		8.20 m	~8.30 m (CH_3)
$[C_7H_7Mo(CO)_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+PF_6^-$	2024 1977	A	4.13 br	2.50	7.27 br	
$[C_7H_7Mo(CO)_2(C_6H_5)_2PC_2H_4As(C_6H_5)_2]^+PF_6^-$	2023 1974	A	4.12 d (2.4)	2.57	7.35 m (PCH_2)	7.32 s ($AsCH_2$)
$[C_7H_7MoCO(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+I$	1958	C	4.62 br	2.42	7.39 br, w	
$[C_7H_7MoCO(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+PF_6^-$	1959	A	4.55 t (2.6)	2.44	7.23 br, w	
$[C_7H_7MoCO(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]^+PF_6^-$	1967	A	4.63 t (2.4)	2.50		2.51 t (13.5) (CH)
$[C_7H_7MoCO(C_6H_5)_2PC_2H_4As(C_6H_5)_2]^+PF_6^-$	1957	A	4.44 d (2.4)	2.47	7.32 m	
$[C_7H_7MoCO(CH_3)_2PC_2H_4P(CH_3)_2]^+PF_6^-$	1934	A	4.40 t (2.6)		8.30 m	~8.30 m (CH_3)
$C_7H_7MoCOC_5H_4NC_2H_4P(C_6H_5)_2I$	1932	C	4.98 d (2.6)	2.38	~7.00 m	1.47 d (5)[f]
$[C_7H_7MoCOC_5H_4NC_2H_4P(C_6H_5)_2]^+PF_6^-$	1960	A	4.62 d (2.6)	2.40	6.83 br, w	1.08 d (5)[f]
$C_7H_7MoCO(C_6H_5)_2SbCH_2Sb(C_6H_5)_2I$	1931	C	4.80 s	2.65	7.55 s	
$C_7H_7MoCOCH_3C[CH_2P(C_6H_5)_2]_3I$	1931	C	4.75 br	2.67	[g]	[g]
$[C_7H_7MoCH_3C[CH_2P(C_6H_5)_2]_3]^+I^-\cdot CH_2Cl_2$		C	4.63 m	2.75	7.65 br	8.47 br (CH_3)[h]
$[C_7H_7MoCH_3C[CH_2P(C_6H_5)_2]_3]^+PF_6^-$		A	4.58 br	2.77	7.58 br	8.52 br (CH_3)
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$[i]		C		2.78	7.92 t (4.0)	
$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$[i]		C		2.73		2.75 t (14.5) (CH)
$(C_6H_5)_2PC_2H_4As(C_6H_5)_2$[i]		C		2.79	7.93 d (4.0) (PCH_2)	7.89 s ($AsCH_2$)
$(CH_3)_2PC_2H_4P(CH_3)_2$[j]		N			8.65 d (8.1)	9.05 d (3.3) (CH_3)
$CH_3C[CH_2P(C_6H_5)_2]_3$		C		2.67	7.50 d (2.8)	9.01 s (CH_3)
$C_5H_4NC_2H_4P(C_6H_5)_2$		C		2.78	7.33 m	1.48 d (4.5)[f]
$(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$[k]		C		2.74	7.96 s	

[a] Run in CH_2Cl_2. [b] Key: br, broad; m, multiplet; s, singlet; d, doublet; t, triplet; w, weak. *J* values (cps) in parentheses. [c] C = chloroform-*d* with tetramethylsilane internal standard; A = acetone-d_6 with hexamethyldisiloxane internal standard; N = neat with tetramethylsilane external standard. [d] Phenyl resonances were asymmetric and complex. [e] C_6H_6 resonance buried under C_6H_5. [f] The 6 proton on the pyridine ring. [g] Too weak and broad to assign with certainty. [h] $\tau(CH_2)$ in CH_2Cl_2 is 4.60 s. [i] R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, 93, 4158 (1971). [j] R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, 26, 1977 (1964). [k] Reference 7.

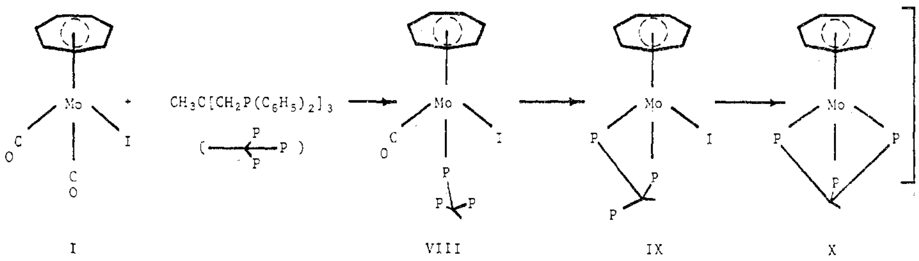

Figure 2.

to "freeze out" the fluxional molecule, there was no change in $\tau(C_7H_7)$ for $C_7H_7Mo(CO)_2$(diphos)I down to $-50°$.

In the monocarbonyls V and VII the one expected ν(CO) band (~1960 cm^{-1}) occurred greater than 100 cm^{-1} above that for similar cyclopentadienyl nonsaline complexes, *e.g.*, in C_5H_5MoCO(diphos)Cl $\nu(CO) = 1845$ cm^{-1}.[12] The decreasing ν(CO) stretching frequencies in the $[C_7H_7MoCO$(ligand)$]^+$ series, ligand = *cis*-diphos (1967 cm^{-1}) > pyphos (1960 cm^{-1}) ≈ diphos (1959 cm^{-1}) ≈ phosars (1957 cm^{-1}) > mdiphos (1934 cm^{-1}), reflect decreasing bonding abilities of the ligands in these compounds. Each of the diphosphine derivatives exhibited a sharp triplet ($J = 2.5$ cps) for the $\tau(C_7H_7)$ resonance due to coupling of the seven equivalent ring protons with the two bonded phosphorus nuclei. An expected doublet ($J = 2.5$ cps) was observed for $\tau(C_7H_7)$ in the monophosphine pyphos and phosars compounds. Evidence of bond formation between the amine and the metal in the pyphos product was determined from the downfield nmr shift in the 6 proton on the pyridine ring from that of the free ligand. Generally, upon bond formation downfield shifts of phenyl, methylene, or methyl resonances from those in the free ligands were observed (Table II).

Because of the inferior withdrawing ability of the *pentahapto*cycloheptatrienyl to the *pentahapto*cyclopentadienyl ring and the excellent bonding potential of the *heptahapto*cycloheptatrienyl system, structure IV is proposed for the saline dicarbonyl derivatives after comparing their ν(CO) stretching frequencies (2025, 1975 cm^{-1}) with those of $[C_5H_5M(CO)_2$(diphos)$]^+PF_6^-$ (1995, 1928 cm^{-1}).[12]

The nonsaline heptahapto configuration III resulting from the reaction of I with pyphos was ascertained from its low conductivity in nitrobenzene, from a comparison of the ν(CO) band (1932 cm^{-1}) with that of the known $C_7H_7MoCO[P(C_6H_5)_3]I$ (1938 cm^{-1}) recorded in CH_2Cl_2,[1] from the $\tau(C_7H_7)$ doublet arising from coupling of the ring protons with the bonded phosphorus atom, and from the invariance of the chemical shift of the 6 proton on the pyridine ring from that of the free ligand.

When I was allowed to interact with the potentially tridentate ligand ($CH_3C[CH_2P(C_6H_5)_2]_3$) in refluxing benzene, a monitoring of the change in ν(CO) stretching frequencies and the isolation of compounds VIII and X indicate the reaction scheme shown in Figure 2 was followed. Of course the chelation of a second phosphine in VIII to displace the iodine as an iodide followed by the rapid chelation of the third phosphine to produce X cannot be discounted.

Registry No. $C_7H_7Mo(CO)_2$(diphos)I, 40832-23-3; $C_7H_7Mo(CO)_2$(*cis*-diphos)I, 40832-24-4; $C_7H_7Mo(CO)_2$(mdiphos)I, 40832-25-5; $[C_7H_7Mo(CO)_2$(diphos)$]^+PF_6^-$, 40904-66-3; $[C_7H_7Mo(CO)_2$(phosars)$]^+PF_6^-$, 39322-75-3; $[C_7H_7MoCO$(diphos)$]^+PF_6^-$, 40832-26-6; $[C_7H_7MoCO$(*cis*-diphos)$]^+PF_6^-$, 40904-67-4; $[C_7H_7MoCO(phosars)]^+PF_6^-$, 40832-27-7; $[C_7H_7MoCO(mdiphos)]^+PF_6^-$, 40832-28-8; $C_7H_7MoCO(pyphos)I$, 40832-29-9; $[C_7H_7MoCO(pyhos)]^+PF_6^-$, 40832-30-2; $C_7H_7MoCO(distib)I$, 39324-46-4; $C_7H_7MoCO(triphos)I$, 39322-77-5; $[C_7H_7Mo(triphos)]^+I^-$, 39322-76-4; $[C_7H_7Mo(triphos)]^+PF_6^-$, 40832-31-3; $C_7H_7Mo(diphos)I$, 39322-74-2; $C_7H_7Mo(phosars)I$, 39322-73-1; $C_7H_7Mo(arsars)I$, 39322-72-0; $C_7H_7MoC_{12}H_8 \cdot N_2I$, 40832-32-4; $C_7H_7MoC_{10}H_8N_2I$, 40832-33-5; diphos, 1663-45-2; *cis*-diphos, 983-80-2; phosars, 23582-06-1; mdiphos, 23936-60-9; triphos, 22031-12-5; pyphos, 10150-27-3; distib, 30224-53-4; $C_7H_7Mo(CO)_2I$, 36580-34-4.

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Contribution from Bell Laboratories,
Murray Hill, New Jersey 07974

Ortho Phenyl Hydrogen Interactions in Bis[1,2-bis(diphenylphosphino)ethane]-Metal Complexes

A. P. GINSBERG* and W. E. LINDSELL

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The ^1H nmr spectra at 30° of the complexes $[Ir(dppe)_2X_2]Cl$ ($X_2 = O_2, S_2, Se_2$), *cis*-$[M(dppe)_2(CO)_2]$ (M = Cr, Mo, W), $[Ir(dppe)_2C_3S_2]Cl$, and *cis*-$[Ru(dppe)_2(CH_3)Cl]$ (dppe = 1,2-bis(diphenylphosphino)ethane) all show a 1:2:1 triplet of intensity 4 protons or, in the case of the last two complexes, two triplets each of intensity 2 protons in the range τ 3.5–4.3. From the decoupling behavior and temperature dependence of the triplets, together with the known X-ray structure of $[Ir(dppe)_2S_2]Cl$, it is shown that they are due to the resonance of certain ortho phenyl hydrogen atoms shifted upfield from the main phenyl multiplet by interaction with the two nonphosphorus cis groups. It is suggested that the presence of such a triplet in the spectrum of a six-coordinate bis(dppe) complex is conclusive evidence for cis geometry, but its absence is only tentative evidence for trans geometry.

Introduction

A recent X-ray structure determination[1] on the complex $[Ir(dppe)_2S_2]Cl$ [dppe = 1,2-bis(diphenylphosphino)ethane] has shown that two ortho phenyl hydrogen atoms are, respectively, 2.54 and 2.57 Å distant from the sulfur atoms, while no other S· · ·H contact in the cation is less than 2.8 Å. It was suggested that there might be a significant interaction between the S_2 ligand and the two closest hydrogens. In this paper we report proton nmr evidence for such an interaction and show that it is present in all of the complexes $[Ir(dppe)_2X_2]Cl$ ($X_2 = O_2$, S_2, and Se_2) as well as $[Ir(dppe)_2C_3S_2]Cl$, *cis*-$[Ru(dppe)_2(CH_3)Cl]$, and *cis*-$[M(dppe)_2(CO)_2]$ (M = Cr, Mo, and W). Furthermore, we find no evidence of ortho phenyl hydrogen interactions in trans isomers of $[M(dppe)_2XY]$ (M = Ir, X = Y = I; M = Ru or Os, X = Y = Cl). Our results therefore suggest a convenient method of distinguishing cis and trans isomers of $[M(dppe)_2XY]$ complexes.

Although the hydrogen-cis-ligand interactions elucidated in the present work exert an important effect on the phenyl region ^1H nmr spectrum, they are much weaker than the ortho phenyl hydrogen-metal interactions found in a number of tertiary phosphine-metal complexes.[2] In particular, there is no evidence of internal addition to the cis ligand or of deuterium exchange with the phenyl hydrogen atoms.

Experimental Section

The following compounds were prepared by the procedure in the reference cited: $[Ir(dppe)_2]Cl$,[3] $[Ir(dppe)_2CO]Cl$,[3] $[Ir(dppe)_2O_2]Cl$,[3] $[Ir(dppe)_2S_2]Cl$,[4] $[Ir(dppe)_2Se_2]Cl$,[4] $[Ir(dppe)_2C_3S_2]Cl$,[5] *cis*-$[Ru(dppe)_2(CH_3)Cl]$,[6] *cis*-$[M(dppe)_2(CO)_2]$ (M = Cr, Mo, W),[7] *trans*-$[Cr(dppe)_2(CO)_2]$,[7] *trans*-$[M(dppe)_2Cl_2]$ (M = Ru, Os).[8] The identity of the products was confirmed by ir spectroscopy and melting point determinations and, where necessary, by microanalysis.

trans-**$[Ir(dppe)_2I_2]Cl$** was prepared by adding dropwise a solution of I_2 (49.5 mg, 0.195 mmol) in methylene chloride (25 ml) to $[Ir(dppe)_2]Cl$ (200 mg, 0.195 mmol) in degassed methylene chloride (15 ml) under N_2. After 2 hr ~100 ml of ether was added to give an orange-yellow precipitate. The product was collected, washed with ether, and dried *in vacuo*, yield 0.20 g (80%). *Anal.* Calcd for $C_{52}H_{48}ClI_2IrP_4$: C, 48.86; H, 3.78; Cl, 2.77; I, 19.86; P, 9.69. Found: C, 48.81; H, 4.25; Cl, 2.65; I, 20.72; P, 9.05. Conductivity measurements over the concentration range 5×10^{-3}–10^{-4} N in acetonitrile solution at 25.0 ± 0.1° confirm the formulation as a 1:1 electrolyte; Λ *vs.* $\sqrt{C}$ gave a linear plot with an intercept $\Lambda_0 = 141$ and a slope $A = 406$ (calcd, 334). Infrared spectra in the range 4000–250 cm^{-1} (CsI disk) showed only bands due to dppe, consistent with Cl^- being the anion. The ^{31}P nmr spectrum of $[Ir(dppe)_2I_2]Cl$ was obtained on a Varian HA-100 at 40.5 MHz with broad-band proton decoupling. The sample, a concentrated solution of the complex in methylene chloride, was in a 5-mm o.d. nmr tube fitted with a coaxial capillary containing 85% H_3PO_4. A search to 8000 Hz on both sides of the phosphoric acid line revealed only a single absorption at δ +6.74 ppm. This supports the assignment of trans geometry to $[Ir(dppe)_2I_2]Cl$.

^1H nmr spectra were determined at 100 MHz with a Varian HA-100 spectrometer and, where necessary, at 300 MHz on an HR-300 machine. On the HA-100, temperatures were measured with a copper-constantan thermocouple; on the HR-300 the temperature was determined from the separation of the CH_3 and OH resonances in spectra of methanol, according to the calibration chart in the Varian manual. ^{31}P–^1H decoupling of the HA-100 spectra was accomplished by irradiating the sample at a nominal frequency of 40.5 MHz with a stabilized Model SD-60 NMR Specialties heteronuclear spin decoupler.

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(1) W. D. Bonds and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 3413 (1972).

(2) See, for example, G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

(3) (a) L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966); (b) A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966).

(4) A. P. Ginsberg and W. E. Lindsell, *Chem. Commun.*, 232 (1971).

(5) A. P. Ginsberg and W. E. Silverthorn, *Chem. Commun.*, 823 (1969).

(6) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 6017 (1963).

(7) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

(8) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961).