properties of both the complexes conform well to eq 2, so that they are likely to be binuclear like the other compounds.

The strength of the antiferromagnetic interaction, or the magnitude of J, is undoubtedly affected by many factors. Our influence which is likely to be of importance is the stereochemistry about the oxygen bridges. The relevance of this factor can be established by an extension of the study to a wider range of the present type of binuclear compounds, which allows great scope for variation of the stereochemistry.

Acknowledgment.—The authors thank Dr. Ernest Challen of this University for the carbon, hydrogen, and nitrogen microanalyses. S. J. G. is grateful for the award of an I.C.I.A.N.Z. Research Fellowship.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Complexes of Trivalent Phosphorus Derivatives. III. Metal Carbonyl Complexes of 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene[1,2]

BY R. B. KING[3] AND K. H. PANNELL[4]

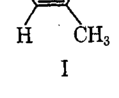
Received August 7, 1967

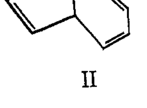
The reactions of various metal carbonyl derivatives with the novel unsaturated tertiary phosphine 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene ($C_8H_8PC_6H_5$) have been investigated. Cycloheptatrienetricarbonylmolybdenum reacts with $C_8H_8PC_6H_5$ at room temperature to give pale yellow *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_3$ where one of the two ligands is bonded to the metal atom through its phosphorus atom and one of its double bonds. In all other complexes of $C_8H_8PC_6H_5$ prepared in this work, only the phosphorus atom of this ligand is bonded to the metal atom. Hexacarbonylchromium reacts with $C_8H_8PC_6H_5$ to form a mixture of $(C_8H_8PC_6H_5)Cr(CO)_5$ and *trans*-$(C_8H_8PC_6H_5)_2Cr(CO)_4$. Hexacarbonylmolybdenum reacts with$C_8H_8PC_6H_5$ to give a mixture of $(C_8H_8PC_6H_5)Mo(CO)_5$ and *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$; however, the latter compound is better prepared from $C_8H_8PC_6H_5$ and cycloheptatrienetricarbonylmolybdenum at 100°. The monosubstituted yellow iron complex $(C_8H_8PC_6H_5)Fe(CO)_4$ may be prepared from $Fe(CO)_5$ and $C_8H_8PC_6H_5$ and the deeper yellow, relatively unstable, disubstituted iron complex *trans*-$(C_8H_8PC_6H_5)_2Fe(CO)_3$ from $Fe_2(CO)_9$ or $C_8H_8Fe(CO)_3$ and $C_8H_8PC_6H_5$. The mercury derivatives $Hg[Fe(CO)_3NO]_2$ and $Hg[Co(CO)_4]_2$ react with $C_8H_8PC_6H_5$ to form orange $Hg[Fe(CO)_2(NO)(C_8H_8PC_6H_5)]_2$ and yellow $Hg[Co(CO)_3(C_8H_8PC_6H_5)]_2$, respectively.

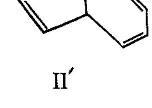
Introduction

Metal carbonyl derivatives of both tricovalent phosphorus compounds[5] and of olefins[6] have received much attention in recent years. However, metal carbonyl complexes of unsaturated phosphines have received much less attention. Interrante, Bennett, and Nyholm[7] have found (2-propenylphenyl)diphenylphosphine (I) to act as a bidentate ligand forming $[C_3H_5C_6H_4P(C_6H_5)_2]M(CO)_4$ (M = Cr, Mo, and W) compounds.

Recently Katz, Nicholson, and Reilly[8] have described the novel unsaturated phosphine 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, $C_8H_8PC_6H_5$ (II, abbreviated as "Ppb"), prepared from phenyldichlorophosphine and dipotassium cyclooctatetraenediide. This ligand is in theory capable of coordinating with a metal atom either as a tertiary phosphine, a monoolefin, or a conjugated diolefin depending on the bridge to which the metal atom is bonded. Furthermore, it is possible that two of the three bridges could coordinate simultaneously to the metal atom resulting in complexes in which the $C_8H_8PC_6H_5$ ligand is bonded to the metal atom either through the diolefin and olefin bridges, through the diolefin and tertiary phosphine bridges, or through the olefin and tertiary phosphine bridges. This paper reports the reactions of $C_8H_8PC_6H_5$ (II) with various metal carbonyl derivatives, especially those where more than one carbonyl group often are replaced with ligands.


I


II


II′

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra (Table II) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 421 or 621 spectrometer. In addition the spectra of the soluble compounds were investigated in the

---

[1] Part II: R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

[2] Portions of this work were presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[4] Postdoctoral Research Associate supported by Grant AF-AFOSR-1211-67 from the Air Force Office of Scientific Research during the period Nov 1966–May 1967.

[5] T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

[6] R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, 77 (1962).

[7] (a) L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, **5**, 2212 (1966); (b) for a recent report of the crystal structure of one of these metal carbonyl complexes of (2-propenylphenyl)diphenylphosphine, see H. Luth, M. R. Truter, and A. Robson, *Chem. Commun.*, 738 (1967).

[8] T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966).

TABLE I

SOME METAL CARBONYL DERIVATIVES OF 9-PHENYL-9-PHOSPHABICYCLO[4.2.1]NONATRIENE[a]

Compound	Color	Mp, °C	Sublimes	Analyses, %									
				C		H		P		O		Metal	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$\mathrm{PpbMo(CO)_5}$	White	128–129	115° (0.2 mm)	50.1	50.5	2.9	2.9	6.9	6.7	17.8	18.2	21.4	21.4
cis-$\mathrm{(Ppb)_2Mo(CO)_4}$	Pale yellow	230 dec	No	60.8	61.4 60.9	4.1	3.8 4.1	9.8	8.1 10.3	10.1	11.4 8.8	15.2	14.8 16.2
cis-$\mathrm{(Ppb)_2Mo(CO)_3}$[c]	Pale yellow	190 dec	No	61.6	61.9	4.3	4.4	10.2	10.6	7.9	6.4	15.9	16.6
$\mathrm{C_7H_8Mo(CO)_2Ppb}$	Red	175 dec	130–150° (0.2 mm)	60.5	60.7	4.6	4.5	6.8	8.5			21.0	18.4
$\mathrm{PpbCr(CO)_5}$	White	129–130	94° (0.05 mm)	56.4	56.3	3.2	2.8	7.7	7.8	19.8	19.8	12.9	12.9
trans-$\mathrm{(Ppb)_2Cr(CO)_4}$	White	270 dec	No	65.3	64.8	4.4	4.6	10.5	10.9	10.9	11.1	8.8	8.8
$\mathrm{PpbFe(CO)_4}$	Yellow	106–107	90° (0.2 mm)	56.8	56.9	3.4	3.3	8.3	7.9	16.8	17.1	14.6	14.8
trans-$\mathrm{(Ppb)_2Fe(CO)_3}$	Yellow[b]	160 dec	No	65.9	64.3 62.7	4.6	4.3 4.6	11.0	10.9			9.9	9.1 9.5
$\mathrm{Hg[Fe(CO)_2NOPpb]_2}$	Orange	167 dec	No	42.3	42.0	2.9	2.7	6.8	7.1	10.6	10.8		
$\mathrm{Hg[Co(CO)_3Ppb]_2}$	Yellow[b]	180 dec	No	44.8	45.2	2.9	2.8	6.8	6.6	10.5	10.6		

[a] Ppb = 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene. [b] These compounds become black upon standing. [c] Molecular weight: calcd, 604; found, 649 (Mechrolab vapor pressure osmometer in benzene solution).

TABLE II

METAL CARBONYL ν(CO) FREQUENCIES OF NEW COMPOUNDS REPORTED IN THIS PAPER[a,b]

Compound[c]	Medium[d]	ν(CO), cm^{-1}
$\mathrm{PpbMo(CO)_5}$	CH	2074 w, 1948 s
$\mathrm{PpbCr(CO)_5}$	CH	2066 w, 1938 s
trans-$\mathrm{(Ppb)_2Cr(CO)_4}$	DM	1936 m, 1880 vs
cis-$\mathrm{(Ppb)_2Mo(CO)_4}$	DM	2021 w, 1907 s, 1871 m
cis-$\mathrm{(Ppb)_2Mo(CO)_3}$	DM	1934 s, 1831 s
	Nujol	1933 s, 1850 m, 1830 m, 1815 m
$\mathrm{C_7H_8Mo(CO)_2Ppb}$	KBr	1895 s, 1805 s
$\mathrm{PpbFe(CO)_4}$	CH	2052 m, 1976 m, 1946 s, 1935 s
trans-$\mathrm{(Ppb)_2Fe(CO)_3}$	DM	1874 s
$\mathrm{Hg[Fe(CO)_2(NO)Ppb]_2}$	DM	1987 w, 1961 m, 1917 s, 1711 m[e]
$\mathrm{Hg[Co(CO)_3Ppb]_2}$	KBr	1991 w, 1937 s

[a] Perkin-Elmer 421 and 621 spectrometers with grating optics were used for these spectra. [b] In addition to the ν(CO) frequencies reported in this table, all of these compounds exhibited the following frequencies (KBr pellets) apparently arising from the $C_8H_8PC_6H_5$ ligand: 1460 (vw), 1440 (vw–w), 1230 (vw), 1105 (vw), 735 (w–m), and 675 (w–m) cm^{-1}. [c] Ppb = 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene. [d] CH = cyclohexane solution; DM = dichloromethane solution; KBr = KBr pellet; Nujol = Nujol mull. [e] ν(NO) frequency.

ν(CO) region in cyclohexane or dichloromethane solutions. Proton nmr spectra (Table III) were taken in chloroform-*d* solutions and recorded on a Varian A-60 spectrometer. In many cases the proton nmr spectra were so complex and the multiplets so poorly resolved that their analysis could not be carried beyond the simple identification of the resonances due to the phenyl protons, the olefinic protons, and the allylic protons.

The ligand 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, $C_8H_8PC_6H_5$, was prepared from phenyldichlorophosphine, cyclooctatetraene, and potassium metal using the procedure described by Katz, Nicholson, and Reilly.[8] When the procedure worked, the yields of distilled $C_8H_8PC_6H_5$ were in the range 30–37%. Occasionally the preparation failed completely for unclear reasons. The product was identified as II rather than II′ from its proton nmr spectrum.[8]

The metal carbonyl derivatives used in this work were either commercial samples[9] or materials prepared by procedures described in "Organometallic Syntheses."[10]

A nitrogen atmosphere was routinely provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admission to evacuated vessels.

Reaction between $C_8H_8PC_6H_5$ and $C_7H_8Mo(CO)_3$. a. In Boiling Methylcyclohexane.—A mixture of 3.0 g (11.0 mmoles) of cycloheptatrienetricarbonylmolybdenum, 3.0 g (14.1 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 250 ml of methylcyclohexane was refluxed at the boiling point for 6 hr. During the course of this reaction impure $(C_8H_8PC_6H_5)_2Mo(CO)_4$ precipitated. At the end of the reaction period this product was filtered while the reaction mixture was still hot giving 1.0 g (42% yield) of crude $(C_8H_8PC_6H_5)_2Mo(CO)_4$. Pure samples of this material for analyses and spectra were obtained as pale yellow crystals, mp 230° dec, by recrystallization from a nitrogen-saturated mixture of dichloromethane and hexane.[11]

After removal of the $(C_8H_8PC_6H_5)_2Mo(CO)_4$ by filtration as described above, the filtrate was cooled to room temperature. The red-brown powder which separated was filtered. This product was then heated in a sublimer at 190° (0.15 mm) to give 0.18 g (3.5% yield) of a red sublimate of $C_7H_8Mo(CO)_2(C_8H_8PC_6H_5)$. Resublimation of this material at 150° (0.1 mm) gave 0.05 g of pure product, mp 175° dec.

In other reactions carried out in a similar manner the yield of $C_7H_8Mo(CO)_2(C_8H_8PC_6H_5)$ was in the range 0–5%.

b. In Hexane at 25°.—A mixture of 0.5 g (1.84 mmoles) of cycloheptatrienetricarbonylmolybdenum, 0.4 g (1.86 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 200 ml of hexane was allowed to react at 25° for 3 hr. The resulting yellow powder was filtered giving 0.35 g of $(C_8H_8PC_6H_5)_2Mo(CO)_3$ (34% yield). This product could be purified further by crystallization from a nitrogen-saturated mixture of dichloromethane and hexane.[11]

If a solution of $(C_8H_8PC_6H_5)_2Mo(CO)_3$ in dichloromethane was treated with carbon monoxide at 25° (1 atm), the infrared spectrum in the ν(CO) region gradually changed over a period of 5–10 hr to that of $(C_8H_8PC_6H_5)_2Mo(CO)_4$. Further treatment of the solution with carbon monoxide produced unknown metal carbonyl derivatives.

Reaction between $C_8H_8PC_6H_5$ and $Mo(CO)_6$.—A mixture of 1.0 g (3.8 mmoles) of hexacarbonylmolybdenum, 0.81 g (3.8

---

[9] Metal carbonyls from the following suppliers were used: $Fe(CO)_5$, Antara Division of General Aniline and Film, New York, N. Y.; $Mo(CO)_6$, Climax Molybdenum Co., New York, N. Y.; $Cr(CO)_6$, Pressure Chemical Co., Pittsburgh, Pa.

[10] The compounds $C_7H_8Mo(CO)_3$, $C_8H_8Fe(CO)_3$, $Fe_2(CO)_9$, $Hg[Co(CO)_4]_2$, and $Hg[Fe(CO)_3NO]_2$ were prepared by procedures given by R. B. King, "Organometallic Syntheses," Vol. I, Academic Press, Inc., New York, N. Y., 1965. The preparation given there for $Fe_2(CO)_9$ (p 93) was made more reproducible by using a specially constructed water-cooled reactor and an immersion-type mercury ultraviolet lamp purchased from Nester-Faust Corp., Newark, Del.

[11] These recrystallizations were carried out by dissolving the complex in dichloromethane, adding hexane to the filtered solution, and then concentrating the solution in a stream of nitrogen until the complex crystallized.

TABLE III

PROTON NMR SPECTRA OF SOME COMPOUNDS REPORTED IN THIS PAPER[a]

	Chemical shifts, τ[d]			
		Olefinic protons		
Compound[b]	Phenyl protons	C=CC=C	C=C	Bridgehead (allylic) protons
Ppb[c]	~2.9	3.84 4.27	4.57 ddd (4.7, 6.3, 11.9)	6.37 ddd (4.7, 7.8, 18.3)
$PpbMo(CO)_5$	~2.9	~3.9 ~4.2	4.55 ddd (1, 3, 12)	6.33 ddd (4, 8, 19)
$PpbCr(CO)_5$	2.5–2.7	3.3–4.4		6.0–6.3
$PpbFe(CO)_4$	2.64, 2.73	3.5–4.3	4.3–4.6	6.2 d (16)
cis-$(Ppb)_2Mo(CO)_4$	2.5–2.8	3.7–4.8		6.5–6.8
$(Ppb)_2Mo(CO)_3$	2.7, 2.73, 2.81 3.0–3.3	3.75–4.55		6.7–6.95
trans-$(Ppb)_2Fe(CO)_3$	2.76	3.6–4.7		6.2 d (18)
$Hg[Fe(CO)_2NOPpb]_2$	2.66, 2.75	3.6–4.3	4.3–4.7	6.13 d (15)
$Hg[Co(CO)_3Ppb]_2$	2.58–2.85	3.5–4.35	4.35–4.62	6.24 d (13)

[a] Varian A-60 spectrometer; $CDCl_3$ solutions. Tetramethylsilane was used as an internal standard. [b] Ppb = 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene. [c] Data of T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88,** 3832 (1966). [d] d = doublet (separations in cps given in parentheses).

mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 250 ml of methylcyclohexane was refluxed at the boiling point for 15 hr. The solution was then filtered while hot. Solvent was removed from the filtrate at ~50° (30 mm) to give 1.2 g of crude brownish $(C_8H_8PC_6H_5)Mo(CO)_5$. This product was then heated at 50–100° (0.15 mm) in a sublimer to remove traces of $Mo(CO)_6$ and $C_8H_8PC_6H_5$. After removing these materials, sublimation was continued at 115° (0.2 mm) to give 0.52 g of white crystalline $(C_8H_8PC_6H_5)Mo(CO)_5$, mp 128–129° (31% yield).

The residue in the sublimer was shown to be $(C_8H_8PC_6H_5)_2Mo(CO)_4$ by examination of the ν(CO) frequencies in its infrared spectrum.

Reaction between $C_8H_8PC_6H_5$ and $Cr(CO)_6$.—A mixture of 1.0 g (4.55 mmoles) of hexacarbonylchromium, 1.0 g (4.70 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 200 ml of methylcyclohexane was boiled under reflux for 36 hr. The solution was filtered while hot to yield 0.1 g of yellow $(C_8H_8PC_6H_5)_2Cr(CO)_4$. Upon cooling the filtrate to room temperature an additional quantity of product precipitated in purer form. A total of 0.27 g (20% yield) of $(C_8H_8PC_6H_5)_2Cr(CO)_4$ was obtained. This product was too insoluble in organic solvents for satisfactory recrystallization or for investigation of its nmr spectrum.

The filtrate from the isolation of $(C_8H_8PC_6H_5)_2Cr(CO)_4$ was freed of solvent at ~50° (30 mm). The waxy yellow solid residue was sublimed at 100° (0.15 mm) to give 0.52 g of slightly impure $(C_8H_8PC_6H_5)Cr(CO)_5$. This was purified by resublimation at 94° (0.1 mm) to give 0.31 g (29% yield) of $(C_8H_8PC_6H_5)Cr(CO)_5$, mp 129–130°.

Reaction between $C_8H_8PC_6H_5$ and $C_8H_8Fe(CO)_3$.—A mixture of 2.0 g (8.2 mmoles) of cyclooctatetraenetricarbonyliron, 2.0 g (9.4 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 250 ml of methylcyclohexane was boiled under reflux for 5 hr. During the course of the reaction yellow $(C_8H_8PC_6H_5)_2Fe(CO)_3$ gradually precipitated. At the end of the reaction period this product (1.5 g) was filtered while the reaction mixture was still hot. Cooling the filtrate yielded additional product (0.3 g) which was likewise filtered. The combined samples of crude $(C_8H_8PC_6H_5)_2Fe(CO)_3$ were recrystallized[11] in portions from nitrogen-saturated mixtures of dichloromethane and hexane to give 1.3 g (78% yield) of yellow $(C_8H_8PC_6H_5)_2Fe(CO)_3$. This compound is very sensitive to air in solution and also in the solid state unless kept cold. Microanalysis was difficult owing to the tendency for the compound to decompose before reaching the analyst.

Ultraviolet irradiation (Pyrex filter) of $C_8H_8Fe(CO)_3$ and $C_8H_8PC_6H_5$ in hexane solution also gave a 70% yield of $(C_8H_8PC_6H_5)_2Fe(CO)_3$.

Reaction between $C_8H_8PC_6H_5$ and $Fe(CO)_5$.—A mixture of 2.2 ml (3.2 g, 16.3 mmoles) of pentacarbonyliron, 1.0 g (4.7 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 150 ml of methylcyclohexane was boiled 18 hr under reflux. At this time the solution was black and contained small particles. It was filtered while hot giving 0.12 g of a mixture of $(C_8H_8PC_6H_5)_2Fe(CO)_3$ and decomposition product, presumably metallic iron. The filtrate was cooled to room temperature. More (0.3 g) yellow $(C_8H_8PC_6H_5)_2Fe(CO)_3$ separated and was removed by filtration. The combined samples of $(C_8H_8PC_6H_5)_2Fe(CO)_3$ were recrystallized[11] from a nitrogen-saturated mixture of dichloromethane and hexane to give 0.17 g (12% yield) of yellow $(C_8H_8PC_6H_5)_2Fe(CO)_3$.

The filtrate from the solution of $(C_8H_8PC_6H_5)_2Fe(CO)_3$ was freed of solvent at ~50° (30 mm). The oily solid residue was sublimed at 100° (0.1 mm) to give an oily yellow sublimate. This sublimate was washed with a minimum quantity of hexane and then resublimed at 110° (0.2 mm) to give 0.8 g (45% yield) of pale yellow $(C_8H_8PC_6H_5)Fe(CO)_4$.

Reaction between $C_8H_8PC_6H_5$ and $Fe_2(CO)_9$.—A mixture of 1.7 g (4.7 mmoles) of enneacarbonyldiiron, 1.0 g (4.7 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 150 ml of pentane was boiled 30 min under reflux. The solution was filtered hot to give 0.44 g (32% yield) of yellow $(C_8H_8PC_6H_5)_2Fe(CO)_3$, identified by the ν(CO) frequencies in its infrared spectrum. No $(C_8H_8PC_6H_5)Fe(CO)_4$ could be isolated from this reaction mixture.

Reaction between $C_8H_8PC_6H_5$ and $Hg[Fe(CO)_3NO]_2$.—A mixture of 1.4 g (2.2 mmoles) of $Hg[Fe(CO)_3NO]_2$, 1.1 g (5.17 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 200 ml of hexane was stirred for 30 min at 25° under ultraviolet irradiation.[12] After this time an orange precipitate had formed. This was removed by filtration to give 1.8 g (75% yield) of $Hg[Fe(CO)_2(NO)(C_8H_8PC_6H_5)]_2$. Pure samples of this material for analyses and spectra were obtained by recrystallization[11] from mixtures of dichloromethane and hexane.

Reaction between $C_8H_8PC_6H_5$ and $Hg[Co(CO)_4]_2$.—A mixture of 1.3 g (2.4 mmoles) of $Hg[Co(CO)_4]_2$, 1.0 g (4.7 mmoles) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, and 200 ml of hexane was stirred for 10 min at ~25° under ultraviolet irradiation.[12] The yellow precipitate which had formed was removed by filtration to give 1.61 g (70% yield) of yellow $Hg[Co(CO)_3(C_8H_8PC_6H_5)]_2$. Pure samples of this material for analyses and spectra were obtained by crystallization[11] from mixtures of dichloromethane and hexane.

The compound $Hg[Co(CO)_3(C_8H_8PC_6H_5)]_2$ is much less stable than $Hg[Fe(CO)_2(NO)(C_8H_8PC_6H_5)_2]$. This cobalt compound is air sensitive in solution and gradually decomposes also in the solid state.

---

(12) Later studies suggest that these reactions proceed equally well in the absence of ultraviolet irradiation.

Discussion

Most of the new compounds described in this paper appear to have the $C_8H_8PC_6H_5$ ligand bonded to the metal atom solely with the phosphorus atom and thus appear to be closely related to the corresponding triphenylphosphine derivatives. Thus the complexes $(C_8H_8PC_6H_5)Fe(CO)_4$ and *trans*-$(C_8H_8PC_6H_5)_2Fe(CO)_3$ appear to be simple substitution products of $Fe(CO)_5$ corresponding entirely to the triphenylphosphine derivatives. The rather unstable complex *trans*-$(C_8H_8PC_6H_5)_2Fe(CO)_3$ could be obtained in better yield from $C_8H_8PC_6H_5$ and either the cyclooctatetraene complex $C_8H_8Fe(CO)_3$ or $Fe_2(CO)_9$. Its *trans* configuration is confirmed by its single strong $\nu(CO)$ frequency at 1874 cm^{-1}.

The reactions of $C_8H_8PC_6H_5$ with $Hg[Fe(CO)_3NO]_2$ and with $Hg[Co(CO)_4]_2$ were carried out in the presence of ultraviolet irradiation hoping to break the transition metal–mercury bond. However, the substitution products $Hg[Fe(CO)_2(NO)(C_8H_8PC_6H_5)]_2$ and $Hg[Co(CO)_3(C_8H_8PC_6H_5)]_2$ were obtained, closely analogous to other substitution products of these mercury derivatives.[13,14]

The products obtained from $C_8H_8PC_6H_5$ and the group VI metal carbonyl derivatives appear to be particularly interesting. Hexacarbonylchromium reacts with $C_8H_8PC_6H_5$ in boiling methylcyclohexane to give two products. The first product is volatile and appears to be $(C_8H_8PC_6H_5)Cr(CO)_5$ where the $C_8H_8PC_6H_5$ ligand has replaced one of the six carbonyl groups of $Cr(CO)_6$. The infrared spectrum of $(C_8H_8PC_6H_5)Cr(CO)_5$ in the $\nu(CO)$ region exhibits a strong band at 1938 cm^{-1} and a weak band at 2066 cm^{-1} corresponding to the E and one of the A_1 modes, respectively, expected for an $LM(CO)_5$ species.[15] As is the case with the triphenylphosphine derivatives $(C_6H_5)_3PM(CO)_5$ the second A_1 mode appears to be hidden under the strong E mode. The second product of composition $(C_8H_8PC_6H_5)_2Cr(CO)_4$ from the reaction between $Cr(CO)_6$ and $C_8H_8PC_6H_5$ is nonvolatile and much less soluble than $(C_8H_8PC_6H_5)Cr(CO)_5$. The infrared spectrum of $(C_8H_8PC_6H_5)_2Cr(CO)_4$ in the $\nu(CO)$ region exhibits a very strong band at 1880 cm^{-1} which corresponds to the expected infrared-active E_u mode for the *trans* isomer. A second much weaker $\nu(CO)$ frequency is observed at 1936 cm^{-1}; this may correspond to the normally infrared-inactive A_{1g} or B_{1g} mode, which could become infrared active because of the asymmetry of the $C_8H_8PC_6H_5$ ligand.

The reaction between $Mo(CO)_6$ and $C_8H_8PC_6H_5$ yields mainly the monosubstituted product $(C_8H_8PC_6H_5)Mo(CO)_5$, a volatile white solid resembling its chromium analog. Minor amounts of the disubstituted product *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$ are also formed. The tendency for molybdenum to form *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$ but for chromium to form *trans*-$(C_8H_8PC_6H_5)_2Cr(CO)_4$ is apparently a consequence of the different sizes of the two metal atoms.

The reaction of $C_8H_8PC_6H_5$ with cycloheptatrienetricarbonylmolybdenum is particularly interesting. At room temperature a pale yellow crystalline precipitate of $(C_8H_8PC_6H_5)_2Mo(CO)_3$ is formed. This is the only compound prepared in this work where $C_8H_8PC_6H_5$ acts as a bidentate ligand. The proton nmr spectrum of this complex (Table III) exhibits two distinctly separated phenyl resonances (one at τ 2.7–2.8 and the other at τ 3.0–3.3) unlike the nmr spectra of any other of the $C_8H_8PC_6H_5$ complexes prepared in this work. This suggests nonequivalence of the $C_8H_8PC_6H_5$ ligands. The $\nu(CO)$ frequencies have the pattern expected for a *cis*-$L_2L'M(CO)_3$ compound where L and L′ have nearly identical π-acceptor strengths. The formula $(C_8H_8PC_6H_5)_2Mo(CO)_3$ indicated by analyses was also confirmed by an osmometric molecular weight determination in benzene solution. These observations lead us to suggest structure III for the complex $(C_8H_8PC_6H_5)_2Mo(CO)_3$. Apparently in this system a tricovalent phosphorus atom and a carbon–carbon double bond have nearly identical π-acceptor strengths.

At higher temperatures (*e.g.*, 100°) $C_8H_8PC_6H_5$ and cycloheptatrienetricarbonylmolybdenum react to form another pale yellow crystalline precipitate of composition $(C_8H_8PC_6H_5)_2Mo(CO)_4$. The infrared spectrum of this material exhibits three $\nu(CO)$ frequencies at 2021 (w), 1907 (s), and 1871 (m) cm^{-1} corresponding to the A_1, B_1, and B_2 modes, respectively, of a *cis*-$L_2M(CO)_4$ molecule. The fourth $\nu(CO)$ frequency, another A_1 mode, expected for a *cis*-$L_2M(CO)_4$ molecule is probably hidden under the strong B_1 mode.

The formation of a molybdenum tetracarbonyl derivative in the reaction of cycloheptatrienetricarbonylmolybdenum is not unprecedented. Tris(dimethylamino)phosphine likewise reacts with $C_7H_8Mo(CO)_3$ to form a tetracarbonyl complex $[((CH_3)_2N)_3P]_2Mo(CO)_4$.[1] In this case the product is the *trans* isomer. However, *cis*-$[((CH_3)_2N)_3P]_2Mo(CO)_4$, recently[16] prepared from $(CH_3SCH_2CH_2SCH_3)Mo(CO)_4$ and tris(dimethylamino)phosphine, has been shown to rearrange to the corresponding *trans* isomer at slightly above room temperature. The formation of *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$ (IV) from $C_7H_8Mo(CO)_3$ and $C_8H_8PC_6H_5$ appears to take place by carbonylation of the low-temperature product *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_3$ (III) with carbon monoxide evolved in side reactions. This possibility is further supported by the observation that the reaction of *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_3$ (III) in dichloromethane solution with carbon monoxide slowly gives the tetracarbonyl *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$ (IV) with apparent displacement of the coordinated double bond of the $C_8H_8PC_6H_5$ ligand by carbon monoxide. A similar, but faster, reaction has been noted by Kaesz, Winstein, and Kreiter,[17] who find

---

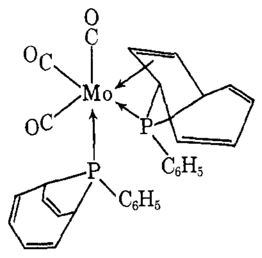
[13] W. Hieber and R. Breu, *Ber.*, **90**, 1259 (1957).

[14] R. B. King, *Inorg. Chem.*, **2**, 1275 (1963).

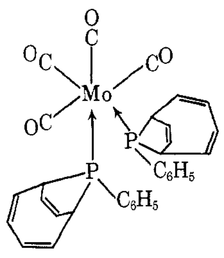
[15] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[16] G. R. Dobson and G. C. Faber, private communication.

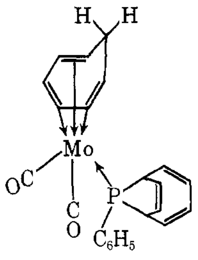
[17] H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Am. Chem. Soc.*, **88**, 1319 (1966).



III



IV



V

the complexes (triene)Mo(CO)$_3$ (triene = 1,3,5-cyclooctatriene or cyclooctatetraene) to react with carbon monoxide for a few minutes at atmospheric pressure to give the tetracarbonyls (triene)Mo(CO)$_4$, where only two of the three double bonds of the triene (those in relative 1,5 positions) remain complexed with the metal atom.

A minor product of the reaction between cycloheptatrienetricarbonylmolybdenum and $C_8H_8PC_6H_5$ is the red sublimable solid, $C_7H_8Mo(CO)_2(C_8H_8PC_6H_5)$ (V), obtained in quantities too small for detailed study. Formation of this complex represents the first example of a reaction of cycloheptatrienetricarbonylmolybdenum with a ligand where the cycloheptatriene ligand is not removed. The relatively low yield of $C_7H_8Mo(CO)_2(C_8H_8PC_6H_5)$ indicates the low tendency for this type of reaction to occur.

This work provides a clear demonstration of the much lower tendency for carbon–carbon double bonds relative to a tricovalent phosphorus atom to bond to a transition metal. Certainly if the double bonds in 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (II) possessed appreciable tendency to bond to a metal atom, chelate complexes of II involving both metal–phosphorus and metal–olefin bonds should be observed. The fact that only one derivative (*i.e.*, *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_3$ (III)) with a metal–olefin bond could be prepared and that the metal–olefin bond in this derivative is readily cleaved by carbon monoxide to form *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$ (IV) demonstrates the lower tendency for metal atoms to bond to olefins than to tricovalent phosphorus atoms. Further work is in progress with vastly different types of unsaturated phosphines in attempts to explore the relative stabilities of metal–olefin and metal–phosphorus bonds in other types of systems.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1211-67 and to Badische Anilin- und Sodafabrik for generous gifts of cyclooctatetraene.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
VICTORIA UNIVERSITY OF WELLINGTON, WELLINGTON, NEW ZEALAND

Metal Complexes of Thiocarbohydrazide

BY G. R. BURNS[1]

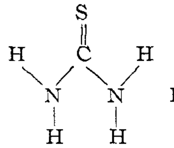
Received August 1, 1967

The ligand thiocarbohydrazide is shown to form a series of complexes with Zn(II), Cd(II), Hg(II), Fe(II), Co(II), Ni(II), Cu(II), and Pd(II). A comparison of their infrared and electronic absorption spectra with the spectra of thiosemicarbazide complexes of known structure suggests that bonding occurs through the thioketo group. Visible reflectance spectra and magnetic moments of the complexes of the first-row transition metal ions and the Mössbauer spectrum of the Fe(II) complex further suggest that they all have strongly distorted octahedral environments.

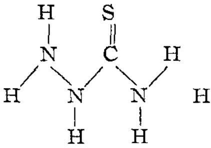
Introduction

A number of ligands with dual sites available for coordination to metal ions have been studied. Of particular interest are thioamide and thiohydrazide derivatives which have both sulfur and nitrogen atoms as potential donors. Two ligands of this type are thiourea (I) and thiosemicarbazide (Htscaz) (II).

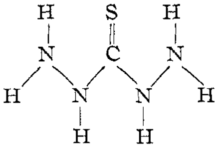
Thiourea acts as a monodentate ligand coordinating to metal ions using only the thioketo group,[2-4] whereas thiosemicarbazide behaves as both a bi- and a monodentate ligand.



I



II



III

X-Ray crystallographic measurements have shown that $Ni(Htscaz)_2SO_4 \cdot 3H_2O$[5] involves coordination by the thioketo group and the NH_2 group of the hydrazine

---

[1] Department of Chemistry, The University, Reading, England.

[2] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

[3] A. L. Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

[4] K. Swaminathan and H. Irving, *J. Inorg. Nucl. Chem.*, **26**, 129 (1964).

[5] R. Grønbaek and S. E. Rasmussen, *Acta Chem. Scand.*, **16**, 2325 (1962).