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Chemistry of the Cyclopentadienylmetal Carbonyls. VI. Reactions of Cyclopentadienylmolybdenum and -tungsten Tricarbonyl Compounds with Phosphine Ligands[1]

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Cyclopentadienylmolybdenum tricarbonyl methyl reacts with triphenylphosphine in donor and hydrocarbon solvents to yield mixtures of the two new compounds $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$ and $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$. In tetrahydrofuran, the mixture of two products results from initial formation of the acetyl derivative with subsequent decarbonylation to yield the methyl compound. The tungsten compound $C_5H_5W(CO)_3CH_3$ is much less reactive to triphenylphosphine substitution. No acetyl substitution product was isolated, but low conversion to $C_5H_5W(CO)_2[(C_6H_5)_3P]CH_3$ occurred. Reaction of $C_5H_5Mo(CO)_3CH_3$ with 1,2-bis(diphenylphosphino)ethane (diphos) afforded the new compound $[C_5H_5Mo(CO)_2COCH_3]_2$-μ-diphos. $C_5H_5W(CO)_3CH_3$ failed to give a bridged derivative with diphos. Cyclopentadienylmolybdenum tricarbonyl dimer reacts with triphenylphosphine in tetrahydrofuran or hexane solution to yield the new compound $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$. The corresponding tungsten dimer does not react even under forcing conditions. Neither $[C_5H_5Mo(CO)_3]_2$ nor $[C_5H_5W(CO)_3]_2$ reacts with diphos under any of the reaction conditions. Physical properties and nmr and infrared spectra of the new compounds are discussed.

Introduction

Reactions of cyclopentadienyliron dicarbonyl methyl with triphenylphosphine have recently been studied under a variety of conditions. In refluxing tetrahydrofuran the only product of this reaction is $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$,[2] while mixtures of the two products $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ and $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ were obtained from the direct reaction in refluxing petroleum ether (bp 90–100°) with ultraviolet irradiation.[3] Under the latter conditions a different mechanism must be involved, because it appears that the methyl derivative is formed first with subsequent carbonylation to afford the acetyl derivative.

We have extended this work in both donor and hydrocarbon solvents to the cyclopentadienylmetal carbonyl methyls of molybdenum and tungsten, $C_5H_5M(CO)_3CH_3$ (M = Mo or W), in order to determine whether the reaction pathways found in the $C_5H_5Fe(CO)_2CH_3$ reactions are of a general nature for cyclopentadienylmetal carbonyl alkyl systems. In addition we studied the effect of ultraviolet irradiation on these reactions. We have also examined reactions of the bidentate phosphorus ligand 1,2-bis(diphenylphosphino)ethane (diphos) with these compounds.

The reactions of $[C_5H_5M(CO)_3]_2$ (M = Mo or W) with triphenylphosphine have also been investigated in a variety of hydrocarbon and donor solvents in an effort to determine the ability of triphenylphosphine to replace carbon monoxide in the cyclopentadienylmetal carbonyls.

Experimental Section

Cyclopentadienylmolybdenum tricarbonyl dimer[4] and cyclopentadienylmolybdenum tricarbonyl methyl[5] were prepared by literature methods. The corresponding tungsten compounds were synthesized by identical routes.[6]

Infrared spectra of the compounds prepared here were recorded on a Beckman IR-10 grating spectrometer. Analyses were conducted by Alfred Bernhardt Laboratories, Mülheim, Germany, and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. (Molecular weights were determined using a Mechrolab vapor pressure osmometer, as approximately 0.05 *m* solutions in benzene.) Infrared and analytical data are reported in Table I. The nmr spectra were recorded on a Varian Associates A-60 spectrometer and are shown in Table II.

Reactions run with ultraviolet irradiation were carried out using a Hanovia 150-w source placed several centimeters away from a quartz flask containing the solution of reactants.

All operations were carried out routinely under an atmosphere of nitrogen, including admission of nitrogen to evacuated flasks and collection of samples under nitrogen during chromatography.

Acid-washed aluminum oxide (Merck) was utilized for chromatographic separations. Tetrahydrofuran (THF) was utilized immediately after distillation over lithium aluminum hydride. All other solvents employed were reagent grade and were used without further purification.

Reaction of $C_5H_5Mo(CO)_3CH_3$ with Triphenylphosphine in Tetrahydrofuran.—$C_5H_5Mo(CO)_3CH_3$ (4.0 g, 15.4 mmoles) and triphenylphosphine (5.0 g, 19.1 mmoles) were refluxed in exactly 200 ml of THF. At 12, 24, and 36 hr 50-ml aliquots were syringed from the reaction vessel. The refluxing of the remaining portion of the mixture was terminated after a total reaction time of 48 hr. The workup of all four fractions was the same. Tetrahydrofuran was removed by rotary evaporator and the resultant solid was taken up in chloroform and filtered. The resultant solution was chromatographed on alumina with a 1:1 mixture of chloroform and hexane as eluent. Three yellow bands were observed and collected. The products from these bands were identified as $C_5H_5Mo(CO)_3CH_3$, $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$, and $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$ in the order of their elution. Crystallization was effected from chloroform–octane mixtures.

The resulting quantities of the products at the different reaction times are shown in Table III. Over-all yields from this

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(1) Previous paper in this series: P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal. Chem.* (Amsterdam), in press.

(2) J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, **5**, 889 (1966).

(3) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *ibid.*, **5**, 1177 (1966).

(4) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., New York, N. Y., 1965, p 109.

(5) See ref 4, p 145.

(6) We are grateful to the Climax Molybdenum Co. for samples of $Mo(CO)_6$ and $W(CO)_6$, precursors of these materials.

TABLE I

PRODUCTS OF THE REACTIONS OF CYCLOPENTADIENYLMOLYBDENUM AND -TUNGSTEN TRICARBONYL DERIVATIVES WITH PHOSPHINE LIGANDS

Compound	Mp,[a] °C	Color	Carbonyl str freq,[b] cm^{-1}		Analysis, % C	H	P	Mol wt
(C$_5$H$_5$)$_2$Mo$_2$(CO)$_5$[(C$_6$H$_5$)$_3$P]	156 dec	Purple	1972 vs, 1895 vs, 1820 s	Calcd	54.48	3.88	4.26	727
				Found	54.33	3.90	3.88	703
C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$	158 dec	Yellow	1940 vs, 1850 vs	Calcd	63.16	4.66	6.28	494
				Found	62.39	4.57	6.55	481
C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$	147 dec	Yellow	1945 vs, 1860 vs, 1605 s	Calcd	62.06	4.43	5.94	522
				Found	61.77	4.54	5.83	512
[C$_5$H$_5$Mo(CO)$_2$COCH$_3$]$_2$-μ-diphos	136 dec	Yellow	1935 vs, 1852 vs, 1600 s	Calcd	57.57	4.36	6.76	918
				Found	56.55	4.57	6.74	929
C$_5$H$_5$W(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$	178 dec	Yellow	1930 vs, 1845 vs	Calcd	53.61	3.94	5.31	582
				Found	51.73	3.90	4.81	570

[a] Determined with a Kofler micro hot stage melting-point apparatus. [b] KBr solution cells (0.1 mm) employed in all cases with chloroform as solvent.

TABLE II

PROTON NMR SPECTRA OF CYCLOPENTADIENYLMOLYBDENUM AND -TUNGSTEN CARBONYL DERIVATIVES PREPARED IN THIS STUDY[a]

Compound		Assignment
(C$_5$H$_5$)$_2$Mo$_2$(CO)$_5$[(C$_6$H$_5$)$_3$P]	2.56 (multiplet)	C$_6$H$_5$
	4.89 (singlet)	C$_5$H$_5$
	5.28 (doublet, J_{PH} = 1.5 cps)[b]	C$_5$H$_5$
C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$	2.61 (multiplet)	C$_6$H$_5$
	5.30 (singlet)[b]	C$_5$H$_5$
	9.61 (doublet, J_{PH} = 2.5 cps)	CH$_3$
C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$	2.57 (multiplet)	C$_6$H$_5$
	4.98 (singlet)[b]	C$_5$H$_5$
	7.38 (singlet)	CH$_3$
C$_5$H$_5$W(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$	2.59 (multiplet)	C$_6$H$_5$
	5.27 (doublet, J_{PH} = 1.5 cps)[b]	C$_5$H$_5$
	9.42 (doublet, J_{PH} = 2.5 cps)	CH$_3$
[C$_5$H$_5$Mo(CO)$_2$COCH$_3$]$_2$-μ-diphos	2.62 (multiplet)	C$_6$H$_5$
	5.12 (singlet)	C$_5$H$_5$
	7.31 (multiplet)	*c*

[a] Deuteriochloroform solutions with TMS as internal standard. [b] The failure of P^{31} to split the C$_5$H$_5$ resonance in all cases is puzzling to us, but this anomaly has been encountered previously.[2,3] [c] Probably arises from accidental overlap of methyl and methylene protons. However, the spectrum was too weak to allow a meaningful integration.

TABLE III

EFFECT OF REACTION TIMES ON THE PRODUCTS[a] OF THE REACTION C$_5$H$_5$Mo(CO)$_3$CH$_3$ + (C$_6$H$_5$)$_3$P IN THF[b]

Time, hr	A, mmole	B, mmoles	C, mmoles
12	0.81	0.47	1.53
24	0.42	1.14	1.38
36	...	1.58	0.79
48	...	2.08	0.59

[a] A = C$_5$H$_5$Mo(CO)$_3$CH$_3$, B = C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$, C = C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$. [b] In all cases, approximately 0.20 g of gray-green noncarbonyl-containing solid was removed by filtration before chromatography.

reaction were: C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$, 2.60 g, 34.2%; C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$, 2.24 g, 28.5%.

Reaction of C$_5$H$_5$Mo(CO)$_3$CH$_3$ with Triphenylphosphine in Hexane.—C$_5$H$_5$Mo(CO)$_3$CH$_3$ (0.8 g, 3.1 mmoles) and triphenylphosphine (1.0 g, 3.8 mmoles) were dissolved in approximately 200 ml of hexane and refluxed with ultraviolet light for 3 hr. The mixture was vacuum filtered while hot, affording approximately 0.25 g, of gray-green noncarbonyl-containing residue and a yellow-orange filtrate. Solvent was removed from the filtrate at aspirator pressure.

The resulting yellow-orange solid was taken up in chloroform–hexane for chromatography in the manner previously mentioned. Upon development of the chromatogram, three yellow bands appeared. From their infrared spectra they were shown to be (in the order of their elution) C$_5$H$_5$Mo(CO)$_3$CH$_3$ (0.07 g), C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$ (0.21 g, 13.8% yield), and C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$ (0.10 g, 6.2% yield).

The reaction was repeated without ultraviolet irradiation with 1.5 g (5.8 mmoles) of C$_5$H$_5$Mo(CO)$_3$CH$_3$ and 2.0 g (7.2 mmoles) of (C$_6$H$_5$)$_3$P in approximately 200 ml of refluxing hexane for 30 hr. Workup identical with that mentioned above afforded 0.30 g of noncarbonyl decomposition product, 0.55 g of C$_5$H$_5$Mo(CO)$_3$CH$_3$, 0.40 g of C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$ (13.1% yield), and 1.22 g of C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$ (34.1% yield).

Decarbonylation of C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$.—C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$ (1.40 g, 2.67 mmoles) was refluxed in approximately 150 ml of THF for 48 hr. Solvent was removed at reduced pressure and the resultant solid was taken up in chloroform and filtered to remove 0.3 g of pale green solid. This solid was insoluble in water, acetone, and hydrocarbon solids, and was discarded. The filtrate was chromatographed on alumina with chloroform–hexane (1:1 mixture).

Three yellow bands were observed to develop. These were collected and crystallized from chloroform–octane. The first fraction (which did not crystallize well) was shown by its infrared spectrum to be C$_5$H$_5$Mo(CO)$_3$CH$_3$ (0.10 g, 0.38 mmole). The second and third fractions were similarly found to be C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$ (0.45 g, 0.91 mmole) and C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]COCH$_3$ (0.36 g, 0.69 mmole), respectively.

Attempted Carbonylation of C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$.—C$_5$H$_5$Mo(CO)$_2$[(C$_6$H$_5$)$_3$P]CH$_3$ (1.0 g, 1.7 mmoles) was refluxed 48 hr in THF while carbon monoxide was slowly bubbled through the solution at atmospheric pressure. Solvent was removed by a rotary evaporator to leave a yellow residue. The infrared spectrum of this residue showed no peak in the 1600-cm^{-1} region attributable to $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$.

The reaction mixture was taken up in chloroform and filtered to remove approximately 75 mg of a gray-green solid. The filtrate was chromatographed on an alumina column with a 1:1 mixture of chloroform–hexane. Two yellow bands were observed, and, after solvent removal and crystallization, these were shown by their infrared spectra to be $C_5H_5Mo(CO)_3CH_3$ (0.10 g) and $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$ (0.65 g) in the order of their elution. No evidence indicating the presence of the acetyl derivative was obtained from chromatography.

Identical results were obtained when this reaction was attempted in refluxing hexane.

Reaction of $C_5H_5W(CO)_3CH_3$ with Triphenylphosphine in Tetrahydrofuran.—$C_5H_5W(CO)_3CH_3$ (1.0 g, 2.9 mmoles) and triphenylphosphine (1.0 g, 3.8 mmoles) were dissolved in approximately 75 ml of tetrahydrofuran and the solution was refluxed for 70 hr. Workup identical with the corresponding molybdenum reaction above afforded 0.1 g of noncarbonyl decomposition product, 0.80 g of $C_5H_5W(CO)_3CH_3$, and 95 mg of $C_5H_5W(CO)_2[(C_6H_5)_3P]CH_3$ (5.7% yield).

The reaction was repeated with the same quantities of both reactants in the higher boiling donor solvents glyme and diglyme. The yield was not substantially improved and decomposition was more extensive than for the reaction in tetrahydrofuran.

Evidence was not obtained for the formation of the acetyl derivative $C_5H_5W(CO)_2[(C_6H_5)_3P]COCH_3$, either from the infrared spectra of samples taken from the reaction vessel at various times or during chromatography.

Reaction of $C_5H_5W(CO)_3CH_3$ with Triphenylphosphine in Hexane.—A solution of 1.4 g of $C_5H_5W(CO)_3CH_3$ (4.0 mmoles) and 1.3 g of triphenylphosphine (5.0 mmoles) in approximately 250 ml of hexane was refluxed with ultraviolet irradiation for 10 hr. Workup was once again identical with that for the corresponding reaction of $C_5H_5Mo(CO)_3CH_3$. Resulting from this reaction were 0.4 g of noncarbonyl decomposition product, 0.28 g of $C_5H_5W(CO)_3CH_3$, and 0.45 g of $C_5H_5W(CO)_2[(C_6H_5)_3P]CH_3$ (21.5% yield). Once again, no acetyl derivative was present among the products.

Shorter reaction times afforded roughly the same yield of $C_5H_5W(CO)_2[(C_6H_5)_3P]CH_3$, but resulted in recovery of larger percentages of $C_5H_5W(CO)_3CH_3$ and in less decomposition.

No reaction was observed in the absence of ultraviolet light.

Reaction of $[C_5H_5Mo(CO)_3]_2$ with Triphenylphosphine in Tetrahydrofuran.—$[C_5H_5Mo(CO)_3]_2$ (2.0 g, 4.1 mmoles) and triphenylphosphine (1.5 g, 5.7 mmoles) were dissolved in approximately 75 ml of tetrahydrofuran. The mixture was refluxed for 24 hr, at which time the reaction was halted and solvent was removed at aspirator pressure. The residue was dissolved in chloroform and filtered to remove 0.2 g of green noncarbonyl solid. The resulting filtrate was placed on an alumina column and eluted with a 1:1 mixture of chloroform and hexane. Two red bands were observed and collected. Solvent was removed from the first fraction, and crystallization was effected from chloroform–octane to yield 0.35 g of $[C_5H_5Mo(CO)_3]_2$. The second fraction was crystallized by a slow passage of nitrogen through the flask to yield 1.80 g of $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ (60.2% yield) as bright purple crystals. This product is extremely light and air sensitive in solution, necessitating chromatography in a semidarkened room. Crystallization was accomplished in a flask wrapped with aluminum foil. In the solid state, however, $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ appears to be stable indefinitely.

Reaction of $[C_5H_5Mo(CO)_3]_2$ with Triphenylphosphine in Hexane.—A solution of 2.5 g of $[C_5H_5Mo(CO)_3]_2$ (5.1 mmoles) and 2.0 g of triphenylphosphine (7.6 mmoles) in approximately 250 ml of hexane was refluxed with ultraviolet irradiation for 2 hr. Longer reaction times were avoided because this led to more extensive decomposition. Workup identical with that for the THF reaction above afforded 0.8 g of gray-green, noncarbonyl decomposition product, 1.1 g of $[C_5H_5Mo(CO)_3]_2$, and 0.8 g of $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ (20.7% yield).

This reaction was also carried out in the absence of ultraviolet light in refluxing hexane for 30 hr. Considerably less decomposition occurred, but only a 6.9% conversion to $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ was obtained.

Attempted Reaction of $[C_5H_5W(CO)_3]_2$ with Triphenylphosphine.—Ultraviolet irradiation of approximately equimolar amounts of $[C_5H_5W(CO)_3]_2$ and $(C_6H_5)_3P$ in hexane solution resulted only in decomposition of the starting materials, even at reaction times as long as 20 hr.

No reaction was observed to occur in refluxing solutions of the donor solvents tetrahydrofuran, 1,2-dimethoxyethane (glyme), or bis(2-methoxyethyl) ether (diglyme), even at reaction times as long as 72 hr.

Reaction of $C_5H_5Mo(CO)_3CH_3$ with 1,2-Bis(diphenylphosphino)ethane in Tetrahydrofuran.—$C_5H_5Mo(CO)_3CH_3$ (1.0 g, 3.8 mmoles) and 1.6 g of diphos (4.0 mmoles) were refluxed in approximately 75 ml of THF for 18 hr. Solvent was removed at reduced pressure. The residue was taken up in chloroform and filtered to remove 0.3 g of noncarbonyl solid. The filtrate was placed on an alumina column and eluted with chloroform. Two yellow bands resulted, and these were collected and solvent was removed. The first band (0.25 g) was shown by its infrared spectrum to be $C_5H_5Mo(CO)_3CH_3$. Crystallization of the solid from the second fraction yielded 0.55 g of yellow powder, which was formulated as $[C_5H_5Mo(CO)_2COCH_3]_2$-μ-diphos (15.8% yield).

Reaction of $C_5H_5Mo(CO)_3CH_3$ with 1,2-Bis(diphenylphosphino)ethane in Hexane.—A solution of 2.6 g of $C_5H_5Mo(CO)_3CH_3$ (10.0 mmoles) and 2.0 g of diphos (5.0 mmoles) in approximately 250 ml of hexane was refluxed for 6 hr with ultraviolet irradiation. Workup identical with that for the THF reaction above gave 0.5 g of noncarbonyl decomposition product, 0.90 g of $C_5H_5Mo(CO)_3CH_3$, and 1.55 g of $[C_5H_5Mo(CO)_2COCH_3]_2$-μ-diphos (16.7% yield).

Attempted Reaction of $C_5H_5W(CO)_3CH_3$ with 1,2-Bis(diphenylphosphino)ethane.—$C_5H_5W(CO)_3CH_3$ (1.05 g, 3.0 mmoles) and diphos (1.2 g, 3.0 mmoles) were dissolved in approximately 75 ml of THF and the solution was refluxed for 36 hr. Solvent was removed at aspirator pressure. The infrared spectrum of the solid residue contained only the characteristic carbonyl bands of $C_5H_5W(CO)_3CH_3$. The residue was taken up in chloroform and filtered to remove 0.1 g of noncarbonyl decomposition product. Chromatography of the filtrate on alumina with chloroform–hexane yielded a single yellow band, which was collected and shown to be $C_5H_5W(CO)_3CH_3$ by its infrared spectrum. Identical results were obtained in the higher boiling solvents glyme and diglyme and in hexane solution with ultraviolet irradiation, except that a higher percentage of decomposition occurred under these more drastic conditions.

Attempted Reactions of $[C_5H_5Mo(CO)_3]_2$ and $[C_5H_5W(CO)_3]_2$ with 1,2-Bis(diphenylphosphino)ethane.—Neither $[C_5H_5Mo(CO)_3]_2$ or $[C_5H_5W(CO)_3]_2$ gave an isolatable substitution product with diphos under conditions identical with those for the corresponding reactions with triphenylphosphine. This was confirmed both by monitoring the reactions by infrared spectra and by the behavior of the reaction products during chromatography.

Discussion

The reactions of alkyl- and arylmetal carbonyls with various ligands have been carefully studied.[7-9] More recently these investigations have been extended to include reactions of cyclopentadienyliron dicarbonyl methyl. Bibler and Wojcicki[2] found that $C_5H_5Fe(CO)_2CH_3$ reacted with a variety of phosphorus ligands in tetrahydrofuran to form exclusively the acetyl derivatives $C_5H_5Fe(CO)(L)COCH_3$ [L = $(C_6H_5)_3P$,

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[7] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3996, 5043 (1964).

[8] T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).

[9] J. Chatt, *J. Chem. Soc.*, 634 (1966).

$(n\text{-}C_4H_9)_3P$, $(C_6H_5O)_3P$, or $(n\text{-}C_4H_9O)_3P]$. These reactions proceeded to a lesser extent in diethyl ether, and in refluxing hexane no reaction was observed to occur. The authors suggested that the ability of the solvent to function as a donor was essential to the reaction.

The reaction of triphenylphosphine and cyclopentadienyliron dicarbonyl methyl was carried out in this laboratory using ultraviolet irradiation of a refluxing petroleum ether (bp 90–100°) solution of these reactants. Both the acetyl and methyl derivatives, $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ and $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ were isolated as products of this reaction.[3] By studying the relative yields of the two products, we concluded that the methyl derivative is the primary reaction product under these conditions; the acetyl compound was formed by a subsequent and facile carbonylation of this compound.

We have now extended our investigations to the systems $C_5H_5M(CO)_3CH_3$ (M = Mo and W) and have found significant differences between the triphenylphosphine substitution reactions of these compounds and the analogous reactions observed to occur with cyclopentadienyliron dicarbonyl methyl.

The reaction of $C_5H_5Mo(CO)_3CH_3$ in refluxing THF solution affords a mixture of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$ and $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$, in contrast to reaction of the iron compound, $C_5H_5Fe(CO)_2CH_3$, which yields only an acetyl substitution product under the same conditions. In order to ascertain whether these products arise by two different reaction pathways, we undertook a study of the effect of reaction time on the relative amounts of each product. The results (Table III) showed an increase in the ratio of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$ to $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$ at longer reaction times. The relative amounts of each product during the course of the reaction suggest strongly that the initial reaction occurs to yield the acetyl derivative only and that this material undergoes a subsequent slow decarbonylation to give the methyl product. In support of this we have also shown that $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$ could be smoothly decarbonylated to $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$ under the reaction conditions employed. Equations 1 and 2 summarize the observed results.

$$C_5H_5Mo(CO)_3CH_3 + [(C_6H_5)_3P] \xrightarrow[65^\circ]{THF} C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3 \quad (1)$$

$$C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3 \longrightarrow C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3 + CO \quad (2)$$

Although $C_5H_5Fe(CO)_2CH_3$ and triphenylphosphine fail to react in refluxing hexane solution, this reaction of $C_5H_5Mo(CO)_3CH_3$ and triphenylphosphine was observed to occur under these conditions. The extent to which the reaction went to completion was not as great in this solvent as in a donor solvent however. After 30 hr approximately 35% of the starting material was recovered whereas at the same time in tetrahydrofuran utilization of starting material was essentially complete. It is unlikely that this difference could be due to temperature variations between the two reactions. More probably there exist two reaction pathways. In the absence of a donor solvent such as THF, one type of reaction can occur; in THF a second, more facile reaction occurs simultaneously. In the latter reaction pathway the solvent may enter into the reaction, perhaps in the same manner proposed by Bibler and Wojcicki.

Interestingly, the relative yields of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$ and $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$ differ depending on the solvent used. After 30 hr the ratio of these two products from the hexane reaction is about 1:3, whereas, for the reaction in THF, a ratio of about 2:1 is found. This observation suggests that the decarbonylation reaction must also be solvent assisted.

The substitution reaction utilizing ultraviolet light is much faster, proceeding to the extent of about 90% in 3 hr. Yields of the desired products were small owing to decomposition, however. The methyl product was formed in substantially larger quantities than the acetyl derivative. Whether a different mechanism is operative here or whether decarbonylation under ultraviolet irradiation is more facile could not be accurately evaluated.

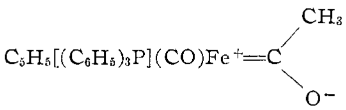
The existence of stable acylmolybdenum compounds of the formula $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$ is impressive in view of the relative instability of the unsubstituted compounds $C_5H_5Mo(CO)_3COR$.[10,11] The latter compounds (R = alkyl) are air sensitive and thermally unstable.[10] Additional stability is often conveyed by substitution of triphenylphosphine for a carbonyl group, as was observed to occur here.

The smooth decarbonylation of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$ in refluxing THF contrasts with the failure to decarbonylate $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ either by refluxing in THF[2] or by ultraviolet irradiation of petroleum ether solutions at reflux (~100°).[3] Failure of the methyl derivative $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$ to add carbon monoxide is also in contrast to the iron system in which the analogous reaction occurs readily.[3]

It seems to us that the iron system results are best interpreted in terms of thermodynamics rather than in reaction rates. The data suggest that the equilibrium (3), analogous to the equilibrium in $RMn(CO)_5$ systems,

$$C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3 + CO \rightleftharpoons C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3 \quad (3)$$

lies far to the right. The higher thermodynamic stability of the acetyl derivative relative to the methyl derivative arises from the additional delocalization of negative charge that can occur to the acyl derivative by an interaction such as



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(10) J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4096 (1963).

(11) R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **2**, 15 (1964).

The shift by 45 cm^{-1} of the ketonic carbonyl stretching frequency on substitution of triphenylphosphine for a carbonyl group in $C_5H_5Fe(CO)_2COCH_3$ supports this.[3]

It is difficult to compare the results observed for the molybdenum and iron systems. Because of the differences in coordination geometries of the two systems, we might find mechanism and rate differences, as well as differences in relative thermodynamic stabilities of the methyl and acetyl compounds. Moreover, the presence of two carbonyl groups relieve somewhat the large back-bonding to the ketonic carbonyl group observed in the iron system. We tend now to discount reaction rates as the determining factor, but rather suggest that different coordination geometry and back-bonding to the ketonic group (which lead to comparable stabilities of the methyl and acetyl compound) are the predominant forces influencing this system.

We have observed a substantially lower chemical reactivity of $C_5H_5W(CO)_3CH_3$ in substitution reactions with triphenylphosphine. In refluxing THF, 80% of the starting material was recovered after 70 hr. Because of extensive decomposition arising at higher temperatures, reactions in higher boiling solvents such as 1,2-dimethoxyethane and bis(1,2-dimethoxyethyl) ether were not satisfactory. No reaction was observed to occur in the nondonor solvent hexane. We have again a clear distinction of the effect of a donor solvent such as THF on the rate of this reaction. As in the substitution reactions of $C_5H_5Fe(CO)_2CH_3$ the use of a donor solvent is necessary to the reaction.

The product of this reaction in THF was exclusively the methyl derivative; no evidence for the acetyl product was seen either on chromatography of the product or on infrared study of the reaction mixture at various times. This result might be explained by assuming that the decarbonylation reaction is rapid relative to the initial formation of an acetyl derivative. However orderly this result might seem when viewed with the molybdenum system, it appears strange that there would exist such a contrast between rates of synthesis and decarbonylation of $C_5H_5M(CO)_2[(C_6H_5)_3P]COCH_3$ for molybdenum and tungsten systems; basically these reactions appear to be similar in many ways.

As in the molybdenum reactions, the ultraviolet reaction of $C_5H_5W(CO)_3CH_3$ and triphenylphosphine was more rapid but it again led to extensive decomposition. The methyl derivative was the only product of this reaction.

Cyclopentadienylmolybdenum tricarbonyl methyl reacts with diphos in either refluxing tetrahydrofuran or in hexane with ultraviolet irradiation to yield the new derivative $[C_5H_5Mo(CO)_2COCH_3]_2$-μ-diphos in low yields. This result is in accord with the fact that for $C_5H_5Mo(CO)_3CH_3$ it is possible to substitute only one carbonyl group by triphenylphosphine. The product of the diphos reaction is structurally analogous to the previously prepared $[C_5H_5Mo(CO)_2I]_2$-μ-diphos and $[C_5H_5W(CO)_2Cl]_2$-μ-diphos.[1] The tungsten compound $C_5H_5W(CO)_3CH_3$ failed to react under the same or more drastic conditions.

In the reaction of $[C_5H_5Mo(CO)_3]_2$ and triphenylphosphine in refluxing THF, a 60% yield of a monosubstitution product $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ was obtained. No evidence of further substitution was found in this reaction. The purple, crystalline product was stable as a solid but solutions were rather light sensitive.

No tungsten analog of the new molybdenum compound $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ could be prepared. In refluxing THF starting material was recovered, whereas in reactions employing more drastic conditions of temperature or time extensive decomposition occurred.

The infrared spectra of the methyl and acetyl derivatives of molybdenum and tungsten prepared here are in accord with the concept of triphenylphosphine being a weaker π acceptor than carbon monoxide. The parent $C_5H_5M(CO)_3R$ compounds exhibit carbonyl absorptions in the ranges 2010–2020 and 1920–1935 cm^{-1}, while the substituted derivatives show absorptions at 1930–1945 and 1845–1860 cm^{-1}. In addition, the acetyl derivatives of molybdenum show a characteristic ketonic carbonyl absorption at 1600 and 1605 cm^{-1}.

The infrared spectrum of $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ may be considered to arise from overlapping spectra of the $C_5H_5Mo(CO)_3$ and $C_5H_5Mo(CO)_2[(C_6H_5)_3P]$ halves of the molecule. The $C_5H_5Mo(CO)_3$ half should afford the spectrum similar to that of $[C_5H_5Mo(CO)_3]_2$, *i.e.*, bands at approximately 1965 and 1920 cm^{-1}. The other should yield a carbonyl pattern similar to other $C_5H_5Mo(CO)_2[(C_6H_5)_3P]X$ derivatives (roughly 1940 and 1840 cm^{-1}) where X in this case is $C_5H_5Mo(CO)_3$. The absorptions of $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ at 1972, 1895, and 1820 cm^{-1} fit this model if the strong, broad absorption at 1895 cm^{-1} is assumed to be two coincident absorptions.

The proton nmr spectra of the compounds reported here are consistent with the failure of triphenylphosphine to remove electron density from the metal atom as well as does carbon monoxide. This is seen in the shift of the cyclopentadienyl resonances to higher field relative to the parent compound. The cyclopentadienyl resonances are (values for unsubstituted compounds in parentheses): $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$, τ 5.30 (4.60);[12,13] $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COCH_3$, τ 4.98 (4.60); $C_5H_5W(CO)_2[(C_6H_5)_3P]CH_3$, τ 5.27 (4.71);[13] $(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$, τ 4.89 and 5.28 (4.61). The somewhat lower C_5H_5 resonance for $C_5H_5Mo(CO)_2[(C_5H_5)_2P]COCH_3$ relative to the molybdenum and tungsten methyl again shows the ability of the acetyl group to "drain" electrons.

The two cyclopentadienyl resonances observed for

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[12] These values were obtained in deuteriochloroform with TMS as internal standard and differ with those of T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956), obtained in toluene at 40 Mc/sec.

[13] H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966), obtained the spectrum of $C_5H_5Mo(CO)_3CH_3$ in chloroform and found values agreeing with our own. These authors found values in toluene for $C_5H_5W(CO)_3CH_3$ in agreement with those of Piper and Wilkinson, and in addition observed splitting of the methyl resonance (τ 9.44) by ^{183}W. We failed to observe this splitting in our study.

$(C_5H_5)_2Mo_2(CO)_5[(C_6H_5)_3P]$ are both shifted from that of $[C_5H_5Mo(CO)_3]_2$; the doublet at τ 5.28 is assigned as arising from the cyclopentadienyl protons on the ring attached to the molybdenum atom which also bears the triphenylphosphine moiety. This conclusion is drawn from both the multiplicity and position of this absorption. The fact that the other resonance is also slightly shifted is probably a reflection of both electronic and steric factors.

The compound $[C_5H_5Mo(CO)_2COCH_3]_2$-μ-diphos decomposes very rapidly in deuteriochloroform solution, precluding a detailed analysis of the nmr spectrum.

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Metal Carbonyl–Phosphorus Trifluoride Systems. IV.[1] Cobalt Nitrosyl Tricarbonyl

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Cobalt nitrosyl tricarbonyl reacts readily with phosphorus trifluoride to yield all possible substitution products of the type $Co(NO)(CO)_x(PF_3)_{3-x}$. This reaction, which can be induced either thermally or by ultraviolet irradiation, always yields mixtures of species which can be separated in high purity by gas–liquid partition chromatography. The pure compounds are reddish liquids that disproportionate slowly at room temperature. The stepwise replacement constants K_1, K_2, and K_3 for the reactions illustrated by the equation

$$Co(NO)(CO)_{4-n}(PF_3)_{n-1} + PF_3 \longrightarrow Co(NO)(CO)_{3-n}(PF_3)_n + CO$$

are 2.7, 0.69, and 0.25. The values are close to the random substitution values of 3.00, 1.00, and 0.33. Both infrared studies and equilibration studies strongly indicate that PF_3 π bonds to about the same degree as carbon monoxide.

Introduction

Cobalt nitrosyl tricarbonyl has been studied as part of a continuing investigation into the interaction of phosphorus trifluoride with metal carbonyls. The remarkable similarity between the ligands carbon monoxide and phosphorus trifluoride has been clearly demonstrated several times. This similarity is shown in both the intermediate compounds[1] and the totally substituted trifluorophosphine complexes which are analogs of metal carbonyls.[1-4]

The use of a compound like $Co(NO)(CO)_3$ provides an opportunity to study not only the remaining carbonyl groups but also the nitrosyl group as the carbon monoxide is being displaced. The isoelectronic similarity between the nitrosyl group and the carbonyl ligand makes an infrared comparison quite reasonable. In addition, the possibility of the replacement of a ligand other than CO can be examined. The substitution of nitrosyl is not, in general, to be expected, but the possibility cannot *a priori* be eliminated.

During the progress of the work, it developed that cobalt nitrosyl tricarbonyl presents an ideal case for an exact study of the distribution of the various $Co(NO)(CO)_x(PF_3)_{3-x}$ species at various $CO:PF_3$ ratios. Cobalt nitrosyl carbonyl yields intermediate substitution compounds readily, and, in addition, these compounds are more clearly separable than the species in systems such as iron, nickel, and molybdenum. Further, the cobalt nitrosyl carbonyl substituents are much less subject to disproportionation than the labile nickel complexes. These advantages make possible a study of the species using vapor–liquid partition chromatography as the analytical tool.

A short report on the preparation of the cobalt nitrosyl complex totally substituted by PF_3 has been published by Kruck[5] but there is no previous information on the intermediates.

The data obtained during the preparation, isolation, and characterization of the compounds in this carbonyl–trifluorophosphine system are reported.

Experimental Section

Cobalt nitrosyl tricarbonyl was prepared several ways using low-pressure synthesis methods. The best approach employed some variations of the method by Gilmont and Blanchard.[6]

The main variations were mechanical ones dealing with the manner of gas absorption and the scale of the reaction. The reaction was carried out in a 3-l., three-neck flask. The center

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(1) Please consider the following references as the previous papers in the series: (a) I. R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964); (b) II. R. J. Clark and E. O. Brimm, *ibid.*, **4**, 651 (1965); (c) III. R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965).

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