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Reactions of Transition-Metal Carbonyls with Organolithium Compounds. III. Synthesis of Tetracarbonyl (Tertiary Phosphite) Oxy- and Amino-Carbene Complexes of the Group VI B Metals[1]

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Compounds of the general composition $M(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)R$ have been synthesized by the reaction of organolithium reagents with $M(CO)_5P(OCH_2)_3CC_2H_5$ under mild conditions, where $M = Cr, Mo, W$; and $R = CH_3, C_6H_5$. Aminolysis of these compounds at -70°C with ammonia and cyclohexylamine have led to the preparation of $M(CO)_4(P(OCH_2)_3CC_2H_5)C(NHR')R$ species, where $M = Cr, Mo, W$; $R = CH_3, C_6H_5$; and $R' = H, C_6H_{11}$. Infrared and proton nuclear magnetic resonance studies have been carried out on these compounds. These carbene *complexes have exclusively* cis *structures with respect to the metal, with the lone exception $Cr(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$, which exists in both* cis *and* trans *isomeric forms. The significance of these stereochemical observations is discussed in terms of the steric and electronic effects involved in the nucleophilic addition reactions of the organolithium reagents with bound carbon monoxide ligands.*

Introduction

The discovery by Fischer and Maasbol[3] that transiton-metal carbonyls undergo nucleophilic addition reactions at the carbon atom of the carbon monoxide ligand with organolithium compounds has led to several stimulating developments in the field of coordination chemistry. These addition products of alkyl- or aryl-lithium reactions with metal carbonyls upon alkylation result in organometallic compounds containing a *carbene* ligand bound to the transition-metal (eq. 1).

$$M(CO)_6 + RLi \rightarrow [M(CO)_5C(O)R]Li \xrightarrow{R'_3OBF_4} M(CO)_5C(OR')R \qquad (1)$$

where M = Cr, Mo, and W.

This procedure has also been extended to the mono-substituted compounds $M(CO)_5E(C_6H_5)_3$ ($M = Cr, Mo, W$; $E = P, As, Sb$) according to the analogous RLi reactions (eq. 2).

$$M(CO)_5E(C_6H_5)_3 + RLi \rightarrow [M(CO)_4(E(C_6H_5)_3)C(O)R]Li \xrightarrow{R'_3OBF_4} M(CO)_4(E(C_6H_5)_3)C(OR')R \qquad (2)$$

The stereochemistry about the metal atom of the substituted metal carbonyl *carbene* compounds produced in equation (2) has been shown to be exclusively the *cis* structure. The result can be explained on the basis of the CO stretching force constant *versus* charge at the carbon atom prediction previously put forth.[1] This assumes electronic effects are dominating over steric effects. Werner and Rascher[4] have independently studied thermal reactions of $Cr(CO)_5C(OR')R$ with tertiary phosphines in hydrocarbon solvent to form *cis* products identical with those prepared *via* equation (2).

In order to further examine our earlier predictions,[1] as well as to study the effects on the metal-*carbene* bond of adding more electron-withdrawing substituents on the metal carbonyl moiety, we have investigated the reactions of $M(CO)_5(P(OCH_2)_3CC_2H_5)$ ($M = Cr, Mo$, and W) with organolithium reagents to procedure metal-carbene compounds.

We also report in this paper the rather interesting reactions (eq. 3) of these phosphite-oxycarbene tetracarbonyl metal compounds with primary and secondary amines to form the corresponding amino carbene

$$M(CO)_4[P(OCH_2)_3CC_2H_5]C(OR')R + RNH_2 \rightarrow M(CO)_4[P(OCH_2)_3CC_2H_5]C(NHR)R \qquad (3)$$

Materials. $Mo(CO)_6$ and $W(CO)_6$ were the generous gift of Climax Molybdenum Company. $Cr(CO)_6$ was purchased from Strem Chemicals, Inc. The metal hexacarbonyls were used without further purification. Organolithium reagents were obtained from Alfa Products. Tetrahydrofuran was distilled over lithium aluminum hydride just before use. Trimethylolpropane phosphine ester was kindly donated by Arapahoe Chemicals, Boulder, Colorado.

Chemical analyses were performed by Meade Microanalytical Laboratory, Amherst, Massachusetts.

Infrared Spectra. Infrared spectra were measured on a Perkin-Elmer 521 spectrophotometer in hexane

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[1] See D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, 9, 1691 (1970) for Part II of this Series.

[2] Petroleum Research Fund Fellow, 1971-72.

[3] E.O. Fischer and A. Maasböl, *Angew. Chem. Internat. Edit.*, 3, 580 (1964); *Chem. Ber.*, *100*, 2445 (1967).

[4] H. Werner and H. Rascher, *Inorg. Chim. Acta*, 2, 181 (1968).

solution. Sample concentrations were in the range 10^{-3} to 10^{-4} molar. One millimeter sodium chloride matching cells calibrated by the interference fringe method were used in the measurements. The spectrophotometer was calibrated with carbon monoxide above 2000 cm^{-1} and with water vapor below 2000 cm^{-1}. The spectral slit with of the instrument was set at 1.5 cm^{-1}. The spectra were measured on an expanded abscissa scale with a scan speed of 15cm^{-1}/minute.

Nuclear Magnetic Resonance Spectra. The proton magnetic resonance spectra were obtained at instrument temperature in deuteriochloroform with tetramethylsilane as internal reference on a Jeolco spectrometer operating at 100MHz.

Calculation of Infrared Band Shapes. Infrared band shapes of the carbonyl stretching vibrations in the substituted metal tetra-carbonyl oxycarbenes have been calculated. The analyses were carried out using a program based on the work of R.N. Jones and J. Pitha of the Division of Pure Chemistry, National Research Council of Canada, and modified for use on the CDC system in our laboratory.[5] The program fits a Cauchy-Gauss product function to an infrared absorption band envelope. Machine calculations were performed on a CDC 6400 at the State University of New York at Buffalo Computing Center.

Preparation of $M(CO)_5(P(OCH_2)_3CC_2H_5)$*, M = Cr, Mo, W.* The substituted metal pentacarbonyl species were prepared photochemically in a quartz vessel under a N_2 atmosphere. A tetrahydrofuran solution containing 4-ethyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.-2]octane ($P(OCH_2)_3CC_2H_5$) and metal hexacarbonyl, in a small molar excess, was irradiated for periods of five to seven hours using a 550 watt Hanovia uv lamp. Solvent was removed at room temperature under reduced pressure. The white colored products were purified by sublimation of the excess metal hexacarbonyls at 40-50° and recrystallization from chloroform-methanol. The compounds were characterized by their infrared spectra in the CO stretching region. Their respective melting points are reported: $Cr(CO)_5(P(OCH_2)_3CC_2H_5)$, 181-183°; $Mo(CO)_5(P(OCH_2)_3CC_2H_5)$, 173-175° (dec.); $W(CO)_5(P(OCH_2)_3CC_2H_5)$, 179-181°. The methyl substituted analogs of these complexes have previously been prepared by Verkade and coworkers.[6]

Preparation of $M(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)R$*, M = Cr, Mo, W; R =* CH_3*,* C_6H_5 *and* $W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)CH_3$*.* The substituted metal tetracarbonyl oxycarbenes were prepared according to the method of Fischer and Aumann[7] with a slight modification: upon dissolving the lithium salt in water, the solution was filtered.[8] Triethyloxonium fluoroborate, the ethylating agent, was prepared as described in the literature.[9] The crystalline carbene complexes were purified by recrystallization from pentane and stored over desiccant at –5°C. Yields were generally greater than 75% for the purified products.

Cis and *trans* $Cr(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$ were partially separated on a basic alumina column using a chloroform-hexane mixture as elutent. An orange-yellow fraction was obtained first which exhibited four bands in the infrared in the region 1970-1850cm^{-1} (due to both *cis* and *trans* isomers). A second yellow colored fraction was obtained which exhibited only the peak at 1939 cm^{-1} (assigned to the *trans* isomer). It was not possible to obtain the separate isomeric products in large yields at this time. The *trans* isomer is estimated to be 20% of the initial reaction product. The reaction was run at least three independent times resulting in identical results.

Preparation of $M(CO)_4(P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})R$*, M = Cr, Mo, W; R =* CH_3*,* C_6H_5 *and* $W(CO)_4(P(C_6H_5)_3)C(NHC_6H_{11})CH_3$*.* Aminolysis reactions were done under a nitrogen atmosphere at dry ice temperature. The $M(CO)_4$(organo-phosphorus ligand)$C(OC_2H_5)R$ species was dissolved with stirring in anhydrous ether and a molar excess of cyclohexylamine ($NH_2C_6H_{11}$) added. A color change was observed within one to five minutes after addition of the amine. The solvent was removed under reduced pressure at room temperature. Upon addition of hexane to the oily product a solid was obtained for all but two products, $Mo(CO)_4(P(OCH_2)CC_2H_5)C(NHC_6H_{11})C_6H_5$ and $W(CO)_4(P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})C_6H_5$. These phenyl carbene derivatives gave only yellow colored oils which were not further purified.

A reaction attempted between $W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)CH_3$ and $NH_2C_6H_{11}$ in refluxing ether gave only a trace of product after 2.5 hours.

Preparation of $W(CO)_4(P(C_6H_5)_3)C(NH_2)CH_3$*.* (a) From $W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)CH_3$: The substituted tungsten tetracarbonyl oxycarbene was dissolved in a stirred solution of tetrahydrofuran maintained at –78°C. Ammonia gas was bubbled through the solution resulting in a color change within two minutes. Solvent was removed under reduced pressure at room temperature. The yellow product was purified by recrystallization from a benzene-hexane solution.

When reaction conditions were changed to room temperature and benzene employed as a solvent, no product was formed when ammonia gas was bubbled through the solution for up to thirty minutes.

(b) From $W(CO)_5C(NH_2)CH_3$: $W(CO)_5C(NH_2)CH_3$ was prepared at room temperature from the oxycarbene species by the previously described procedure.[10] Under a nitrogen atmosphere a hexane solution containing $W(CO)_5C(NH_2)CH_3$ (in slight molar excess) and $P(C_6H_5)_3$ in a quartz vessel was irradiated for 1.5 hours with a 550 watt Hanovia uv lamp. Solvent was removed under reduced pressure at room tem-

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(5) R.N. Jones and J. Pitha, Bulletin No. 12, National Research Council of Canada, 1968, and references contained within.

(6) J.G. Verkade, R.E. McCarley, D.G. Hendricker, and R.W. King., *Inorg. Chem.*, *4*, 228 (1965).

(7) E.O. Fischer and R. Aumann, *Chem. Ber.*, *102*, 1495 (1969).

(8) M.Y. Darensbourg and D.J. Darensbourg, *Inorg. Chem.*, *9*, 32 (1970).

(9) H. Meerwin, *Org. Syn.*, *46*, 113 (1966).

(10) U. Klabunde and E.O. Fischer, *J. Amer. Chem. Soc.*, *89*, 7141 (1967).

Table I. Physical Properties and Analytical Data.

Compound	Color	Mp, [a]°C	% Calcd C	% Calcd H	% Calcd N	% Found C	% Found H	% Found N
$Cr(CO)_4P(OCH_2)_3CC_2H_5)C(OC_2H_5)CH_3$	bright yellow	74-6	42.22	4.81	—	41.93	4.62	—
$Cr(CO)_4P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$	reddish orange	89-90	49.57	4.60	—	49.64	4.62	—
$Cr(CO)_4P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})CH_3$	yellow	114-20	47.89	5.81	3.10	47.74	5.90	3.43
$Cr(CO)_4P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})C_6H_5$	tan-yellow	93-96	53.80	5.50	2.73	53.62	5.60	2.86
$Mo(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)CH_3$	mustard yellow	81-3	38.01	4.33	—	38.31	4.82	—
$Mo(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$	brownish orange	78-80	45.25	4.20	—	45.36	4.44	—
$Mo(CO)_4(P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})CH_3$	pale yellow	104-110	43.74	5.80	2.83	44.46	5.30	2.83
$Mo(CO)_4(P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})C_6H_5$	yellow oil	—	49.56	5.06	2.52	—	—	—
$W(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$	bright yellow	93-5	31.72	3.61	—	31.73	3.75	—
$W(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)CH_3$	orange	84-5	38.53	3.57	—	38.83	3.62	—
$W(CO)_4(P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})CH_3$	tan-yellow	112-5	37.07	4.49	2.40	36.21	4.66	2.74
$W(CO)_4(P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})C_6H_5$	yellow oil	—	42.81	4.37	2.17	—	—	—
$W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)CH_3$	bright orange	129	49.55	3.68	—	49.53	3.81	—
$W(CO)_4(P(C_6H_5)_3)C(NH_2)CH_3$	yellow	170-2	47.94	3.35	2.33	48.50	3.34	2.52
$W(CO)_4(P(C_6H_5)_3)C(NHC_6H_{11})CH_3$	dark yellow	143-6	52.72	4.42	2.05	52.54	4.68	2.01

[a] uncorrected.

Table II. Infrared Spectral Data for $M(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)R$ [a].

Compound		$A_1^{(2)}$	$A_1^{(1)}$ [b]	B_1 [b]	B_2 [b]
$R = CH_3$	Cr	2026.1	1941.8	1911.6	1934.2
	Mo	2035.6	1946.6	1919.3	1935.5
	W	2033.1	1940.7	1912.5	1931.6
$R = C_6H_5$	Cr	2027.6	1946.9	1911.0	1928.4
	Mo	2036.6	1952.0	1918.4	1942.0
	W	2034.6	1945.8	1911.3	1936.8
$W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)CH_3$		2019.1	1924.9	1894.9	1912.4

[a] Frequencies are accurate to ± 0.5 cm^{-1} and were observed in hexane solution. [b] These frequencies were obtained from Cauchy-Gauss product function band shape analyses.

Table III. Infrared Spectral Data for $M(CO)_4(P(OCH_2)_3CC_2H_5)C(NHC_6H_{11})R$ [a].

Compound		$A'^{1}_{(2)}$	$A'_{(1)}$	B_1	B_2 [b]
$R = CH_3$	Cr	2017	1929	1908	1890 sh
	Mo	2026	1934	1914	1895 sh
	W	2023	1925	1905	1890 sh
$R = C_6H_5$	Cr	2021	1938	1916	1896 sh
	Mo	2028	1940	1917	1905 sh
	W	2026	1936	1914	1896
$W(CO)_4(P(C_6H_5)_3)C(NH_2)CH_3$		2010	1900	1890	1880 sh
$W(CO)_4(P(C_6H_5)_3)C(NHC_6H_{11})CH_3$		2009	1910	1885	n.o.

[a] Frequencies are accurate to ± 1 cm^{-1}, except shoulders, which are accurate ± 3 cm^{-1} and were observed in hexane solution. [b] sh = shoulder, n.o. = not observed (buried beneath B_1 band).

perature and the phosphine substituted product was purified as described above.

Results and Discussion

Phosphite derivatives of metal tetracarbonyl oxy- and amino-carbenes are air-stable, generally crystalline solids whose colors range from pale yellow to deep reddish-orange. The compounds are slightly soluble in saturated hydrocarbons, and quite soluble in benzene, chloroform, and carbon disulfide. The compounds are fairly stable in solution for extended periods of time. Table I contains physical properties and analytical data for all complexes prepared in this study.

The *cis* isomers of $M(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)R$ are formed exclusively from the reaction of the metal pentacarbonyl phosphite with RLi, with the possible exception of the phenyl *carbene* derivative of chromium. This structural assignment is consistent with the presence of four carbonyl stretching vibrations ($2A_1+B_1+B_2$) in the infrared spectra (Table II). The pattern of infrared frequencies and intensities is similar to that observed in $Cr(CO)_4[P(C_6H_5)_3]C(OCH_3)CH_3$[4] which has been shown to have a *cis* structure by X-ray crystal structure analysis.[11] Similarly, the $M(CO)_4(P(OCH_2)_3CC_2H_5)C(NHR')R$ are

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(11) O.S. Mills and A.D. Redhouse, *J. Chem. Soc.* (A), 1274 (1969).

assigend a *cis* configuration on the basis of their infrared spectra in the carbonyl stretching region (Table III).

The reaction of $Cr(CO)_5P(OCH_2)_3CC_2H_5$ with phenyllithium, followed by ethylation, results in a *carbene* compound which appears to be a mixture of *cis* and *trans*-$Cr(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$. An infrared spectrum of this product consists of a high-frequency band at $2027.6 cm^{-1}$ with a weak shoulder at $2035 cm^{-1}$ in addition to a set of four closely grouped bands in the region $1950\text{-}1900 cm^{-1}$ (Figure 1). The band at $1939.6 cm^{-1}$ and the weak shoulder absorption at $2035 cm^{-1}$ are assigned to the *trans* isomer while the remaining four bands listed in Table II are ascribed to the *cis* compound. Chromatographic separation of the two isomeric compounds was attempted on a basic alumina column yielding only a partial separation. However, it was very clear from these separation attempts that there were two species present in solution as manifested by changes in the intensity of the infrared band at $1939 cm^{-1}$ relative to the other absorptions. In fact, in one instance, as noted in the Experimental Section, a yellow band was eluted which shown only the $1939 cm^{-1}$ band in the infrared spectrum. In addition, repeated elemental analyses of the product, including molecular weight determinations,[12] indicated the composition to be that for $Cr(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$. The nmr spectrum, however, showed only one set of resonance ascribable to the $-C(OC_2H_5)C_6H_5$ ligand. From an analysis of the relative areas under the calculated infrared band shapes (Figure 1) the percentage of *trans* isomer was estimated to be approximately 20%.

The fact that the equatorial carbon monoxide ligand in $M(CO)_5P(OCH_2)CC_2H_5$ (M = Cr, Mo. W) is the site of reaction is consistent with the proposal of nucleophilic attack ocucrring at the carbon site with the larger CO stretching force constant.[1] The Cotton-Kraihanzel[13] force constants for the CO vibrations in these compounds are: M = Cr, $k_1 = 15.85$ and $k_2 = 16.11$; M=Mo, $k_1 = 15.88$ and $k_2 = 16.19$; M=W, $k_1 = 15.79$ and $k_2 = 16.11$ mdynes/Å, where k_1 and k_2 refer to the axial and equatorial CO stretching force constants, respectively. This proposal assumes electronic effects to be dominant over steric requirements. It is interesting to note that the one case where some axial carbonyl atack is observed involves the smallest metal atom (Cr) and the larger nucleophile (C_6H_5Li). At the same time the difference in the force constants in the cromium pentacarbonyl phosphite complex, k_1 and k_2, has decreased from their difference in $Cr(CO)_5P(C_6H_5)_3$.[1] It seems reasonable to conclude that the balance between electronic effects and steric requirement is becoming more subtle in the addition reaction of phenyllithium to $Cr(CO)_5P(OCH_2)_3CC_2H_5$. It is expected that as the k_1 and k_2 values approach equality the steric requirement will become important.[14] It is, however, of interest to note in this connection that the Tolman cone angle[15] for the phosphite derivative is considerablv less than that of triphenylphosphine; 101 ± 2° versus 145 ± 2°.

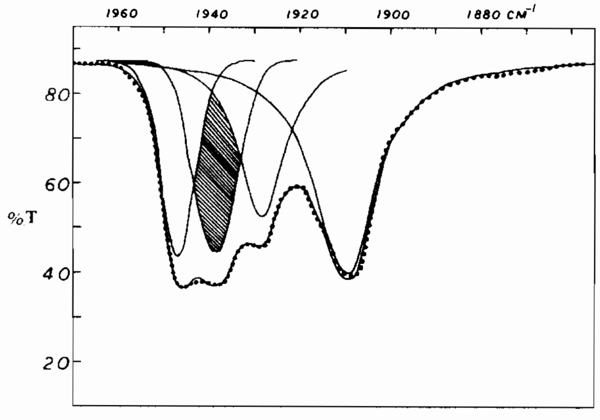

Figure 1. The observed and calculated infrared band shapes in hexane solution for the product mixture of $Cr(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)C_6H_5$. The shaded band (at $1939.6 cm^{-1}$) is attributed to the *trans* isomer. High-frequency carbonyl absorptions are omitted in this drawing: o, observed; —, calculated.

C. G. Kreiter has observed a mixture of *cis*- and *trans*-substituted carbene tetracarbonylphosphine chromium complexes with bulky phosphines such as tricyclohexylphosphine.[16] In these cases, a cis-trans equilibrium is found to occur. However, the rate of isomerization is very slow at room temperature.

E. O. Fischer and co-workers[17] have reported the reactions of $Cr(CO)_5C(OCH_3)C_6H_5$ with primary amines to give the aminophenylcarbene complexes $Cr(CO)_5C(NHR)C_6H_5$ in nearly quantitative yields. However, no detailed reports have yet appeared in the literature on the reaction of substituted transition-metal tetracarbonyl *carbene* compounds with amines.[18] We have found that the $M(CO)_4(P(OCH_2)_3CC_2H_5)C(OC_2H_5)R$ compounds prepared in this study readily react with primary amines at −78°C to quantitatively form aminocarbene compounds. No products were observed from reactions carried out at room temperature. These observations regarding the temperature dependence of this aminolysis are in agreement with the negative Arrhenius activation energy observed by Werner, Fischer, Heckl, and Kreiter[19] for the reaction of $Cr(CO)_5C(OCH_3)C_3H_5$ with primary amines. These workers have performed a detailed mechanistic study

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(12) The molecular weight was determined osmometrically in chloroform and found to always be within 3% of the expected value. It has been pointed out by a reviewer that the band at $1939.6 cm^{-1}$ may be due to an impurity, *trans* $Cr(CO)_4[P(OCH_2)_3CC_2H_5]_2$. However, we have independently prepared *trans* $Cr(CO)_4[P(OCH_2)_3CC_2H_5]_2$, and based on physical and infrared spectral (1937.0 and $2041.4 cm^{-1}$) properties it is possible to conclude that the second component from the reaction of phenyllithium with $Cr(CO)_5P(OCH_2)_3CC_2H_5$ is not the *trans* phosphite species. We are, however, thankful for the suggestion.

(13) F.A. Cotton and C.S. Kraihanzel, *J. Amer. Chem. Soc.*, *84*, 4432 (1962).

(14) A yield of 20% *trans* isomer would be expected if the two type of carbonyl groups were sterically and electronically equivalent.

(15) C.A. Tolman, *J. Amer. Chem. Soc.*, *92*, 2956 (1970). The «cone angle» has been defined by Tolman as the apex angle of a cone centered on the metal atom, just large enough to enclose the van der Waals radii of the outermost atoms of the ligand. These were determined from measurements made on atomic models.

(16) C.G. Kreiter, ACS Division of Inorganic Chemistry Summer Symposium, 1972, Buffalo, New York.

(17) E.O. Fischer, B. Heckl, and H. Werner, *J. Organometal. Chem.*, *28*, 359 (1971).

(18) A report of the reaction between $C_5H_5Mo(CO)(NO)[C(OCH_3)C_6H_5]$ and $HN(CH_3)_2$ leading to the formation of $C_5H_5Mo(CO)(NO)[C(N(CH_3)_2C_6H_5]$ has recently been published; E.O. Fischer and H.J. Beck, *Chem. Ber.*, *104*, 3101 (1971). See also, E. Moser and E.O. Fischer *J. Organometal. Chem.*, *16*, 275 (1969).

(19) H. Werner, E.O. Fischer, B. Heckl, and C.G. Kreiter, *J. Organometal. Chem.*, *28*, 367 (1971).

Table IV. ^{1}H Nmr Spectral Data for $M(CO)_4(P(OCH_2)_3CCH_2CH_3)C(OC_2H_5)R$ compounds.

R	Chemical Shift δ p.p.m. Cr	Mo	W	multiplicity	assignment [b]
CH_3	0.78	0.79	0.80	T	$CCH_2\mathit{CH}_3$
	1.14	1.15	1.16	Q	$C\mathit{CH}_2CH_3$
	1.50	1.50	1.49	T	$OCH_2\mathit{CH}_3$
	2.80 [c]	2.77	2.74	S	CH_3
	4.04	4.05	4.07	D	OCH_2
	4.78	4.78	4.68	Q	$O\mathit{CH}_2CH_3$
C_6H_5	0.80	0.78	0.78	T	$CCH_2\mathit{CH}_3$
	1.16	1.14	1.15	Q	$C\mathit{CH}_2CH_3$
	1.51	1.57	1.56	T	$OCH_2\mathit{CH}_3$
	4.06	4.04	4.06	D	OCH_2
	4.70	4.94	4.80	Q	$O\mathit{CH}_2CH_3$
	7.01	7.20	7.18	m	C_6H_5

[a] Chemical shift (δ) relative to TMS = 0.0 p.p.m. [b] Assignment made on basis of splitting pattern and relative intensities. [c] The singlet methyl peak of the Cr analog was shown under high resolution to be split into a doublet by the phosphorus atom; the coupling constant being 0.016 p.p.m. We thank Dr. M.Y. Darensbourg (Tulane University) for recording this spectrum.

of this reaction and have shown it to involve a series of equilibrium steps which are favored at lower temperatures. The reactions reported in this communication indicate the temperature effect to be *extremely* pronounced in the case of the substituted metal carbonyl *carbene* compounds, since the analogous reactions of the unsubstituted metal *carbene* compounds readily occur at the boiling point of ether.

Nmr Spectra. Peak positions, splitting patterns, and assignments are tabulated in Table IV.

The downfield shift of the methylene quartet of the ethoxy group relative to ordinary $-\mathit{CH}_2OH$ protons in organic molecules is indicative of the electron-withdrawing character of the *carbene* carbon. The shifts are, however, not as large as those observed for the unsubstituted metal pentacarbonyl *carbene* compounds.[8] Similar upfield shifts for the other proton resonances of the *carbene* ligands in the phosphite substituted species relative to those in the corresponding pentacarbonyls are observed. This is presumably due to the fact that the phosphite ligand is less electron-withdrawing when compared with the carbon monoxide group.

The chemical shifts of the phosphite ligand are only slightly affected by complex formation. A measurable downfield shift occurs on going from free $P(OCH_2)_3CCH_2CH_3$ to the $M(CO)_5P(OCH_2)_3CCH_2CH_3$ complex. For example, the resonance positions in $P(OCH_2)_3CCH_2CH_3$ occur at 3.86(D), 1.12(D), 1.12(Q) and 0.78(T); whereas, the corresponding values in $Mo(CO)_5P(OCH_2)_3CCH_2CH_3$ are found at 4.10(D), 1.20(Q) and 0.82(T) for the $O\mathit{CH}_2$, $C\mathit{CH}_2CH_3$ and $CCH_2\mathit{CH}_3$ protons, respectively. As shown in Table IV, these chemical shifts in the *carbene* compounds are again shifted upfield in the phosphite substituted *carbene* compounds relative to the pentacarbonyl phosphite species. This is indicative of the greater electron-withdrawing ability of the carbon monoxide ligand versus the *carbene* ligand.

Infrared Spectra. *cis* $M(CO)_4LL'$ compounds are ideally of C_s symmetry resulting in four infrared-allowed CO stretching modes, two of symmetry A′ and two of symmetry A″. These formally correspond to the $2A_1+B_1+B_2$ modes in the C_{2v} symmetry species where L = L′, and the bands are assigned in this manner in Table II and III. The bands were assigned on the basis of their relative intensities[20] and on approximate Cotton-Kraihanzel force constant calculations, assuming the molecules to be of C_{2v} symmetry. The restriction that $k_2 > k_1$ was applied in these calculations.[21]

Table II indicates that the CO vibrations in the phosphite substituted oxycarbene metal tetracarbonyls occur at higher frequencies than the corresponding values in the phosphine compounds. This is to be expected since phosphites are assumed to be better π acceptor ligands than phosphines. In addition, the CO frequencies in Table III illustrate that the aminocarbenes are less π accepting and/or greater σ donating than the oxycarbene ligands.

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(20) C.L. Hyde and D.J. Darensbourg, *Inorg. Chem.*, in press, May 1973.

(21) k_1 and k_2 are the force constants for the carbonyl groups in the plane and perpendicular to the plane containing the L ligands, respectively.