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The Synthesis of Tetracarbonyl(tertiary phosphine)-methoxycarbenechromium Complexes

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Compounds of the general composition cis-$Cr(CO)_4(PR_3)C(OCH_3)R'$ *have been synthetised by reacting* $Cr(CO)_5C(OCH_3)R'$ ($R'=CH_3$, C_6H_5) *and tertiary phosphines under very mild conditions. The complexes* trans-$Cr(CO)_4(PR_3)_2$ *are formed as by-products in these reactions. The spectroscopic data obtained for the complexes are in full agreement with the proposed structures. It appears that the donating properties of the methoxycarbene ligands are of comparable magnitude to those of triaryl phosphines.*

Introduction

The recent discovery of alkoxycarbene-metal complexes containing the moiety C(OR)R′ as a ligand system[1] has opened a new section in the field of coordination chemistry. As yet the most thoroughly investigated alkoxycarbene-metal complexes are the compounds $M(CO)_5C(OR)R'$ which are conveniently prepared by reaction of the metal hexacarbonyls with lithium alkyls or aryls and further treatment of the resultant ionic derivatives $[M(CO)_5COR']Li$ with trialkyloxonium salts.[2] More recently this synthetic procedure has also been applied to the mono-substituted compounds $M(CO)_5EPh_3$ (M=Cr, Mo, W; E=P, As, Sb; Ph=C_6H_5) according to the following reaction scheme:[3]

$$M(CO)_5EPh_3 \xrightarrow{+LiR'} [M(CO)_4(EPh_3)COR']Li \xrightarrow[-OR_2,\,-LiBF_4]{+[OR_3]BF_4} M(CO)_4(EPh_3)C(OR)R' \qquad (1)$$

In this manner the triphenyl-phosphine, -arsine, and -stibine complexes were obtained. It has also been independently shown that the compounds $Cr(CO)_4(EPh)_3C(OCH_3)CH_3$ (E=P, As, Sb) are accessible from the reaction between $Cr(CO)_5C(OCH_3)CH_3$ and EPh_3 in a non-polar hydrocarbon solvent.[4]

In connection with our previous kinetic and preparative investigations on substitution reactions of Group VI b metal carbonyl compounds[5] we were interested to get some more information about the course of the reaction of pentacarbonylmethoxycarbenechromium complexes with different tertiary phosphines. The present paper reports the preparation and spectroscopic characterisation of *cis*-tetracarbonyl(tertiary phosphine)methoxycarbenechromium complexes and of some *trans*-$Cr(CO)_4(PR_3)_2$ derivatives.

Experimental Section

The starting compounds $Cr(CO)_5C(OCH_3)R'$ ($R'=CH_3$, C_6H_5) were prepared according to the method of Aumann and Fischer[2] and identified by their infrared and n.m.r. spectra. The phosphines $P(C_6H_{11})_3$ and $P(n\text{-}C_4H_9)_3$ were a gift from the Deutsche Advance Production GmbH. Triphenylphosphine was purchased from Fluka and recrystallised from methanol. $P(C_2H_5)_3$ and $P(C_2H_5)_2C_6H_5$ were prepared by standard methods. All operations, except the handling of the solid complexes, were carried out in a pure nitrogen atmosphere. Chromatographic separations were carried out on oxygen-free Merck alumina, neutral, activ. III.

The infrared spectra in the 3-15 mμ region were measured with a Perkin-Elmer spectrometer, Model 21, with LiF optics, and in the far-infrared region with a Beckmann IR 12 grating instrument. A Varian A60 spectrometer was used to obtain the n.m.r. spectra and an Atlas CH 4 instrument for the mass spectra.

General Procedure for the Synthesis of cis-$Cr(CO)_4(PR_3)C(OCH_3)CH_3$. In a 150-ml, two-necked, round-bottom flask fitted with a nitrogen inlet and a reflux condenser, 0.5 g $Cr(CO)_5C(OCH_3)CH_3$ (2.0 mmole) and ~2.2 mmole of the phosphine dissolved in 50 ml hexane were stirred at 55° for 6 hours. The progress of the reaction was determined by infrared spectroscopy. When no more starting material could be detected part of the solvent was removed in *vacuo*. After standing for some hours in an ice bath, yellow crystals precipitated which were filtered off and washed with pentane. After recrystallisation from hexane or toluene-hexane, their composition corresponded to $Cr(CO)_4(PR_3)_2$ (see Table I).

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(2) R. Aumann and E. O. Fischer, *Angew. Chem.*, *79*, 900 (1967); *Angew. Chem. internat. Edit.*, *6*, 879 (1967).

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(4) U. Klabunde, Doctorate Thesis, Northwestern University Evanston, Illinois, 1967; U. Klabunde and E. O. Fischer, unpublished results.

(5) H. Werner and R. Prinz, *Z. Naturforsch.*, *22b*, 260 (1967); *Chem. Ber.*, *99*, 3582 (1966); *Chem. Ber.*, *100*, 265 (1967); *J. Organometal. Chem.*, *5*, 79 (1966); H. Werner, *Angew. Chem.*, *80*, (1968), in press.

The red solution obtained after filtration of the yellow solids was chromatographed in hexane. In general, a fast-running very intense red band and a slow-running bright yellow band were observed, the latter containing the phosphine substituted carbonyl derivatives $Cr(CO)_5PR_3$ and $Cr(CO)_4(PR_3)_2$. From the red fraction the solvent was removed in *vacuo* and the solid products recrystallised from pentane at −40°. Elemental analysis and melting points are given in Table I.

Table I. Compounds obtained from $Cr(CO)_5C(OCH)_3)CH_3$ and tertiary phosphines

Complex	Yield (%)	M.p. (°C) [a]		Analyses %C	%H	%Cr	%P	Mol. wt. [b]	CO bands (cm^{-1}) [c]
$Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)CH_3$	54	117 (dec.)	Calcd.	59.73	7.82	10.35	6.16	502	
			Found	59.85	7.85	10.43	5.92	495	
$Cr(CO)_4[P(C_4H_9)_3]C(OCH_3)CH_3$	46	54	Calcd.	53.76	7.84	12.25		424	
			Found	54.10	8.09	12.27		428	
$Cr(CO)_4[P(C_2H_5)_3]C(OCH_3)CH_3$	22	44-45	Calcd.	45.88	6.22	15.28		340	
			Found	46.32	6.43	15.02		340	
$Cr(CO)_4[P(C_2H_5)_2C_6H_5]C(OCH_3)CH_3$	64	56.5	Calcd.	52.58	5.45	13.42	7.98	388	
			Found	52.86	5.54	13.40	7.64	375	
$Cr(CO)_4[P(C_6H_{11})_3]_2$	22	185 (dec.)	Calcd.	66.27	9.18	7.17		725	1862
			Found	67.04	9.23	6.81		725	
$Cr(CO)_4[P(C_4H_9)_3]_2$	10	65-67	Calcd.	59.14	9.57	9.15		569	1876
			Found	59.73	9.72	8.77		545	
$Cr(CO)_4[P(C_2H_5)_3]_2$	27	57	Calcd.	48.00	7.55	12.99		400	1877 [d]
			Found	48.30	7.48	12.39		384	

[a] Uncorrected. [b] Osmometric in benzene. [c] In cyclohexane. [d] The infrared spectrum of this compound has already been reported, see: R. Poilblanc and M. Bigorgne, *Bull. Chim. Soc. France,* 1301 (1962).

Preparation of cis-*$Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)C_6H_5$.* This complex was prepared in an analogous manner to the corresponding phosphine substituted methoxymethylcarbene derivatives. Thus 0.63 g $Cr(CO)_5C(OCH_3)C_6H_5$ (2.0 mmole) and 0.56 g $P(C_6H_{11})_3$ (2.0 mmole) reacted at 45° to give a 52% yield of the desired complex as dark brown-red crystals (m.p. 114-15°) after repeated chromatography in benzene and recrystallisation from hexane.

Anal. Calcd. for $C_{30}H_{41}O_5PCr$: C, 63.81; H, 7.32; Cr, 9.21. Found: C, 63.23; H, 7.24; Cr, 9.28.

Preparation of trans-*$Cr(CO)_4[P(C_6H_{11})_3]_2$ from* cis-*$Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)CH_3$.* 0.5 g (1.0 mmole) $Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)CH_3$ and 0.5 g (1.75 mmole) $P(C_6H_{11})_3$ were dissolved in 50 ml benzene and refluxed for two hours. During this time the colour of the solution had changed from red to bright yellow. After filtration and removal of the solvent in *vacuo,* a yellow solid was obtained. Two recrystallisations from a benzene-hexane solution gave the pure product (0.56 g) in 74% yield. M.p. 185° (dec.). For analytical data see Table I.

Results and Discussion

(A) cis-*$Cr(CO)_4(PR_3)C(OCH_3)R'$.* Pentacarbonyl methoxycarbenechromium complexes are typified by their pronounced reactivity towards nucleophilic agents. For example, they react with primary and secondary amines,[4,6-8] hydrazines,[3,9] thiophenol,[6] selenophenol[10] and isonitriles[3,11] either by replacement of the methoxy group of the carbene ligand or by nucleophilic addition of the particular donor to the $C_{carbene}$ atom followed by rearrangement. Tertiary phosphines appear, as yet, to be the only donors which lead to substitution of a CO group from these carbene complexes. Most remarkably, the reaction according to equation (2)

$$Cr(CO)_5C(OCH_3)R' + PR_3 \rightarrow Cr(CO)_4(PR_3)C(OCH_3)R' + CO \quad (2)$$

proceeds under very mild conditions, *e.g.,* in the temperature range of 40-60° in a hydrocarbon solvent. Compared to the inertness of the various compounds $Cr(CO)_5L$ (where L represents CO, PR_3, $P(OR)_3$, AsR_3, SbR_3, or CNR) the carbene complexes have been shown to be relatively labile and appear to behave similarly to the halogenopentacarbonylmetal anions $[Cr(CO)_5X]^-$ [12,13] From our kinetic studies on the reaction of $Cr(CO)_5C(OCH_3)R'$ with phosphines[14] it appears that the labilising effect of the carbene ligand is due to an unusual stabilisation of the transition state by the methoxycarbene residue. Thus the high activity should be considered as a kinetic phenomenon which does not reflect on the thermodynamic stability of the starting complexes.

The tetracarbonyl phosphine methoxycarbenechromium compounds described in the Experimental Section are all obtained as diamagnetic red crystals which are fairly stable to air and extremely soluble in organic solvents. The *cis* isomers are formed exclusively. This structural assignment is entirely consistent with (a) the occurence of four CO stretching modes

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$(2A_1 + B_1 + B_2)$ in the infrared spectra, and (b) the obvious similarity of the positions and the intensities of these bands with those obtained for the compound $Cr(CO)_4[P(C_6H_5)_3]C(OCH_3)CH_3$ (see Table II) which has been shown to have a *cis* structure by an X-ray crystal structure analysis.[15]

Table II. C–O stretching frequencies of the complexes $Cr(CO)_4(L)C(OCH_3)R'$ (in hexane)

R′	L	Frequencies, $cm^{-1\,a}$			
CH_3	$P(n\text{-}C_4H_9)_3$	2010 m	1922 sh	1909 s	1893 vs
CH_3	$P(C_2H_5)_3$	2010 m	1921 sh	1909 s	1892 vs
CH_3	$P(C_2H_5)_2C_6H_5$	2009 m	1923 sh	1910 s	1893 vs
CH_3	$P(C_6H_5)_3$ [b]	2014 m	1927 s	1908 sh	1897 vs
CH_3	$P(OC_2H_5)_3$ [c]	2017 m	1918 s	1907 vs	1899 sh
CH_3	$P(C_6H_{11})_3$	2007 m	1929 m	1895 vs	1877 s
C_6H_5	$P(C_6H_5)_3$ [c]	2016 m	1927 s	1910 sh	1899 vs
C_6H_5	$P(C_6H_{11})_3$	2012 m	1905 vs	1890 s	1875 s

[a] Band intensities: w=weak, m=medium, s=strong, vs=very strong, sh=shoulder. [b] From ref. (3). [c] Compound not isolated, spectrum taken from a kinetic run.

With regard to the band shape of the infrared spectra in the ν(C–O) region, it seems noteworthy that in the case of the tricyclohexylphosphine complexes one of the carbonyl bands is shifted to somewhat lower wave numbers (~1875 cm^{-1}). Since the compounds of the general composition *trans*-$Cr(CO)_4(PR_3)_2$ were characterised by one intense C–O stretching frequency at 1860-1890 cm^{-1} [16] (also see Table I), it was originally assumed that an isomeric mixture of *cis*- and *trans*-$Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)R'$ was obtained. There are some observations, however, which do not support this view: (a) the n.m.r. spectra of the complexes show very sharp signals due to the methoxy and methyl ($R'=CH_3$) protons of the carbene moieties; (b) the intensity ratio of the four C–O bands of $Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)R'$ is always the same independent of whether the reaction of $Cr(CO)_5C(OCH_3)R'$ and $P(C_6H_{11})_3$ is run at 60° or at room temperature; (c) all attempts to separate the products by repeated chromatography have failed. It thus appears that the lower position of this particular C–O frequency is possibly due to steric effects caused by the bulky cyclohexyl groups.

In connection with the data shown in Table II, it should furthermore be noted that in general the carbonyl bands of the complexes *cis*-$Cr(CO)_4(PR)_3C(OCH_3)R'$ and *cis*-$Cr(CO)_4(PR_3)_2$ (*e.g.*, $R=C_6H_5$) appear at approximately the same wave lengths. This observation is also true for the compounds $Cr(CO)_5C(OCH_3)R'$ and $Cr(CO)_5P(C_6H_5)_3$ (see Table III). If one accepts the idea[17] that it is the σ-bonding ability of a ligand L which mainly determines the C–O stretching frequencies of a substituted metal carbonyl, one has to conclude that the donor strength of the groups $C(OCH_3)R'$ and $P(aryl)_3$ are of comparable magnitude. This assumption certainly supports the concept developed by Fischer and Maasböl[1] regarding the nature of the metal-to-carbene bond.

Table III. Comparison of the C–O stretching frequencies of isostructural methoxycarbene and triphenylphosphine chromium complexes (in hexane)

	L	Frequencies, cm^{-1}			
$Cr(CO)_5L$:	$C(OCH_3)CH_3$	2066	1987	1963	1949
	$C(OCH_3)C_6H_5$	2064	1988	1965	1955
	$P(C_6H_5)_3$	2070	1989		1945
cis-$Cr(CO)_4(PPh_3)L$:	$C(OCH_3)CH_3$	2014	1927	1908	1897
	$C(OCH_3)C_6H_5$	2016	1927	1908	1897
	$P(C_6H_5)_3$ [a]	2017	1925	1907	1895

[a] In CCl_4; compound prepared from $C_7H_8Cr(CO)_4$ (C_7H_8= norbornadiene) and $P(C_6H_5)_3$: H. Werner and R. Prinz, unpublished results.

Table IV summarises the infrared data obtained in the 1400-150 cm^{-1} region. The C–OCH_3, O–CH_3, and C–C stretching vibrations of the carbene ligands are only slightly different for the pentacarbonyl and tetracarbonyl complexes. In contrast to the spectra of the starting materials $Cr(CO)_5C(OCH_3)R'$, the spectra in the far-infrared of the tricyclohexylphosphine compounds are considerably more complex. The bands between 150 and 520 cm^{-1} may be assigned to the Cr–C and Cr–P stretching modes. Since the concept of bonding in metal carbonyls predicts an increase in the M–C bond order with increasing ligand donating properties, it would be anticipated that the Cr–C stretching frequencies of the carbene phosphine tetracarbonyls should appear at higher wave numbers than those of the carbene pentacarbonyls and also that these occur at higher wave numbers than that of chromium hexacarbonyl. The spectral data seem to be consistent with this expectation: whereas the unsubstituted $Cr(CO)_6$ exhibits a strong Cr–C stretching vibration (species F_{1u}) at 441 cm^{-1},[19] the most intense bands of $Cr(CO)_5C(OCH_3)C_6H_5$ (species E) occur at 463 cm^{-1} and of $Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)R'$ (species B_1) at 478 ($R'=C_6H_5$) and 488 ($R'=CH_3$) cm^{-1}, respectively. With respect to the above mentioned similarity of the position of the ν(C–O) bands of isostructural carbene and triarylphosphine carbonyl chromium complexes, it might be anticipated that the same be observed for the ν(Cr–C) modes. In fact, the most intense band of $Cr(CO)_5P(C_6H_5)_3$ appears at 462 cm^{-1},[20] thus reinforcing the proposed comparison.

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Table IV. Infrared spectra of the complexes $Cr(CO)_4(L)C(OCH_3)R'$ in the range 1400-150 cm^{-1} (in Nujol)[a]

	$R'=CH_3$			$R'=C_6H_5$		
L: CO[b]	$P(n\text{-}C_4H_9)_3$	$P(C_2H_5)_2C_6H_5$	$P(C_6H_{11})_3$	CO[b]	$P(C_6H_{11})_3$	Band assignm.
1348 s	1342 m		1348 m			
1252 s	1215 vs	1235 vs	1205 vs	1224 s	1242 m 1233 m	$\nu(C_{carb}-O)$
1170 s	1156 s	1181 s	1174 s 1152 vs	1178 m 1136 m	1168 m	
1101 s	1092 s	1098 s	1104 s	1074 w	1103 s	
	1049 w	1042 m				
1019 s	1020 m	1027 m	1022 s			$\nu(H_3C-O)$
	986 m	986 m	1004 s	982 s	995 m	
952 m			969 w		935 m	
895 s	898 s	897 s	896 vs	874 s	884 s	$\nu(C_{carb}-C)$
			850 s			
			846 s			
			820 m		826 m	
	772 m	773 m		758 s	760 m	
	736 m	752 m	734 s			
	721 s	731 s	729 s			
		696 s		698 s	703 m 672 s	$\delta(Cr-C-O)$
			566 s	592 s 559 w		
			525 m	534 w	520 s	
			510 s		508 s	
			488 vs	463 vs	478 vs	$\nu(Cr-C)$
			442 s	436 sh	454 sh 431 m	
			404 s		404 s	
			390 s	396 m	392 s	
			341 m			
297 w			264 w		287 w	
			208 w		203 w	$\nu(Cr-P)$
			202 w		198 w	

[a] Frequencies in cm^{-1}; for band intensities see Table II. [b] From refs. (1) and (18).

Data in the literature concerning the position of the $\nu(M-P)$ frequencies are fairly conflicting and until recently only a few assignments had been made. By analogy with the work of Chalmers, Lewis and Whyman[20] it seems quite conceivable that the weak absorptions observed for $Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)R'$ in the 200 cm^{-1} region are due to the Cr–P stretching modes.

The n.m.r. spectra of the phosphine methoxycarbene complexes are reported in Table V. The chemical shifts of the methoxy and methyl protons depend slightly on the nature of the phosphine coordinated to the metal. The reason for the differences is as yet not understood.

Table V. ^1H n.m.r. spectra of the carbene ligands of the complexes $Cr(CO)_4(L)C(OCH_3)R'$ (τ-values in C_6D_6, TMS as internal standard)

			assignment	
R′	L	$O-CH_3$	$C_{carbene}-CH_3$	$C_{carbene}-C_6H_5$
CH_3	CO[a]	6.28	7.67	
CH_3	$P(n\text{-}C_4H_9)_3$	6.24	7.39	
CH_3	$P(C_2H_5)_3$	6.23	7.40	
CH_3	$P(C_2H_5)_2C_6H_5$	6.55	7.79	
CH_3	$P(C_6H_{11})_3$	5.93	7.16	
C_6H_5	CO[a]	6.22		3.05
C_6H_5	$P(C_6H_{11})_3$	6.19		2.83

[a] From ref. (1).

The mass spectra of the compounds prepared show fragmentation patterns similar to those of other substituted metal carbonyls. The ions $[Cr(CO)_4(PR_3)C(OCH_3)R']^+$, $[Cr(CO)_3(PR_3)C(OCH_3)R']^+$, $[Cr(CO)_2(PR_3)C(OCH_3)R']^+$, $[Cr(CO)(PR_3)C(OCH_3)R']^+$, $[Cr(PR_3)C(OCH_3)R']^+$, and $[CrPR_3]^+$ have been observed indicating that the carbonyl groups are first lost in a stepwise manner. The $Cr-C_{carbene}$ bond is then broken in preference to the $Cr-PR_3$ bond.

(B) trans-*Cr(CO)₄(PR₃)₂*. The phosphine carbene tetracarbonyls react with excess phosphine not by substitution of a second CO group but by displacement of the carbene ligand to give the bis(tertiary phosphine) tetracarbonyls.

$$Cr(CO)_4(PR_3)C(OCH_3)R' + PR_3 \longrightarrow Cr(CO)_4(PR_3)_2 + \{C(OCH_3)R'\} \qquad (3)$$

The bright yellow crystalline diamagnetic compounds of formula $Cr(CO)_4(PR_3)_2$ are also obtained as by-products in the reaction of $Cr(CO)_5C(OCH_3)R'$ and PR_3 (see Experimental Section), the yields strongly depending both upon the phosphine and the reaction conditions employed. Some preliminary kinetic studies on the reaction of $Cr(CO)_4[P(C_6H_{11})_3]C(OCH_3)CH_3$ and $P(C_6H_{11})_3$ suggest that the bis(tertiary phosphine) complexes are formed by an S_N2-type mechanism, probably with a direct attack by the phosphine on the formally divalent $C_{carbene}$ atom. Although the fate of the carbene fragment has not been entirely elucidated it may be assumed that it reacts with the attacking phosphine to form a substituted phosphine-methylene compound.

The infrared spectra of $Cr(CO)_4(PR_3)_2$ in the ν(C–O) region (see Table I) show only one single sharp band clearly indicating a *trans* configuration for the complexes. This structural result which is probably attributed to steric effects parallels the recent work of Dobson and Houk[21] who report the formation of *trans*-$CrCO)_4[P(OC_2H_5)_3]_2$ from the reaction of *cis*-2,5-dithiahexanchromium tetracarbonyl and triethylphosphite.

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