Journal of Organometallic Chemistry, 64 (1974) 239—244
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

TRANSITION METAL CHEMISTRY

VIII. SYNTHESIS AND IR STUDY OF MONOSUBSTITUTION PRODUCTS OF $Cr(CO)_6$ AND TERTIARY SUBSTITUTED ARYL GROUP VB DERIVATIVES

F.T. DELBEKE * and G.P. VAN DER KELEN

Laboratory for General and Inorganic Chemistry-B, University of Ghent, Krijgslaan 271, B-9000 Ghent (Belgium)

(Received May 8th, 1973)

Summary

The synthesis of a series of compounds of general formula $LCr(CO)_5$ is presented, the ligands employed being aryl Group VB derivatives of formulae $(C_6H_5)_3E$ and (4- or $3\text{-}XC_6H_4)_3E$ with $E = P$, As, Sb and $X = Cl$, F. The ν(M—C) and δ(M—C—O) frequencies in the IR spectra have been assigned and are discussed. An assignment of the ^{12}CO and ^{13}CO stretching fundamentals is also given. A possible explanation is presented for the anomalies observed in the ν(CO) spectrum and the CO frequency shifts are discussed in terms of σ and π bonding.

As a further development of the transition metal carbonyl chemistry started a few years ago in this laboratory [1,2], and in an attempt to provide additional information regarding bonding and structure of Group VB derivatives, the synthesis of some substitution products of metal carbonyls and a series of these new tertiary substituted aryl Group VB compounds has been undertaken. An infrared spectral study of the carbonyl stretching frequencies is discussed together with the M—C—O deformation and M—C stretching regions of the spectrum.

I. Synthesis

The common method for synthesizing compounds of the type $LM(CO)_5$ is that developed by Magee et al. [3]. In this method the reactants are refluxed in diglyme until all the hexacarbonyl has been consumed. With $Cr(CO)_6$, however, the authors have mentioned that disubstituted compounds of the type *trans*-$L_2Cr(CO)_4$ are apparently preferred; the reaction of $Cr(CO)_6$ with the ligand in

---

[*] Present address: Laboratory for Pharmacology and Toxicology, Casinoplein 24, B-9000 Ghent (Belgium).

TABLE 1

PHYSICAL AND INFRARED DATA FOR $LCr(CO)_5$ COMPOUNDS

L in $LCr(CO)_5$	Reaction time (h)	Temp. (°C)	Melting point (°C)	Frequencies in cm^{-1}		
				$\nu(CO)^c$	$\delta(MCO)^c$	$\nu(MC)^c$
$(C_6H_5)_3P$	1.5	150^a	128.5	2062.7s, 2055.2(sh), 1981.2w, 1942.3vs	671, 654, 547	464, 418
$(4\text{-}FC_6H_4)_3P$	4	140^a	125–129	2064.3s, 2057.0(sh), 1982.7w, 1952.4(sh) 1943.7vs, 1911.7vw	671, 658, 543	466, 412
$(3\text{-}FC_6H_4)_3P$	72	75^b	124	2065.6s, 2058.2(sh), 1985.0w, 1954.4(sh) 1945.6vs, 1914.3vw, 1901.4vw	670, 652, 544	472, 409^d
$(4\text{-}ClC_6H_4)_3P$	4	110^a	158–160	2064.9s, 2057.4(sh), 1984.0w, 1953.8(sh) 1945.0vs, 1913.0vw, 1899.2vw	670, 655, 540	461, 428, 417
$(3\text{-}ClC_6H_4)_3P$	2.5	150^a	127–129	2065.9s, 2058.5(sh), 1985.8w, 1955.3(sh) 1946.7vs, 1914.0vw, 1905.0vw	670, 651, 556	476
$(C_6H_5)_3As$	72	80^b	135	2064.2s, 2056.4(sh), 1982.2w 1944.5vs, 1915.5vw, 1903.9vw	672, 653, 546	474, 417
$(4\text{-}FC_6H_4)_3As$	3.5	140^a	107–109	2065.6s, 2058.5(sh), 1983.9w, 1951.6(sh) 1945.8vs, 1908vw, 1897vw	671, 653, 547	461
$(3\text{-}FC_6H_4)_3As$	72	$75–80^b$	96	2066.7s, 2059.3(sh), 1985.6w, 1947.4vs	670, 651, 543	459
$(4\text{-}ClC_6H_4)_3As$	72	100^b	153–155	2066.0s, 2058.2(sh), 1984.6w 1951.5(sh), 1946.3vs, 1912vw	671, 653, 545	460
$(3\text{-}ClC_6H_4)_3As$	72	$75–80^b$	123	2066.8s, 2058.9(sh), 1986.2w 1952.2(sh), 1947.8vs	670, 651, 544	459
$(C_6H_5)_3Sb$	72	$75–80^b$	133.6	2061.5s, 2054.0(sh), 1981.6w, 1944.7vs, 1915.6vw, 1889.0vw	672, 654, 540	462
$(4\text{-}FC_6H_4)_3Sb$	77	$75–80^b$	130.8	2063.1s, 2057.0(sh), 1984.0w, 1955.3(sh), 1946.7vs, 1913.6vw	672, 653, 541	463
$(3\text{-}FC_6H_4)_3Sb$	77	$70–80^b$	111.2	2064.3s, 1985.2w, 1956.9(sh) 1948.4vs, 1916.8vw	671, 651, 542	463
$(4\text{-}ClC_6H_4)_3Sb$	77	$75–80^b$	170	2063.4s, 2056.0(sh), 1983.0w 1957.1(sh), 1947.5vs, 1916.5vw	671, 651, 540	462
$(3\text{-}ClC_6H_4)_3Sb$	77	$75–80^b$	116	2064.4s, 2057.0(sh), 1985.2w 1957.4(sh), 1949.3vs, 1917w	670, 650, 549	462

[a] Diglyme. [b] Dioxane. [c] Cyclohexane. [d] Raman.

diglyme as a solvent resulting in a mixture of mono- and di-substitution products in most cases. Although a method for separating these compounds has been published [4], in this study syntheses have been carried out under well-defined conditions for each ligand so that a high yield of the monosubstitution product $LCr(CO)_5$ has been obtained.

Thus, a mixture of $Cr(CO)_6$ and L was refluxed in an appropriate solvent (the molar ratio $Cr(CO)_6/L$ being approximately 2/1 and 1/1 in dioxane and diglyme respectively). After reaction, the solution was filtered over alumina, evaporated in vacuo and the residue recrystallized from warm n-hexane yielding yellow, green or orange crystalline $LCr(CO)_5$ compounds as confirmed by their IR spectrum in the CO stretching region.

Physical data relating to these new derivatives are given in Table 1 where the infrared data for $Ph_3PCr(CO)_5$, $Ph_3AsCr(CO)_5$ and $(4\text{-}FC_6H_4)_3PCr(CO)_5$ are included for comparative purposes only. It was found, however, that with $Cr(CO)_6$ and L [5,6,7], where L is a fluoro- or chloro-substituted tertiary arylbismuthine, as the starting materials it was not possible to synthesize $LCr(CO)_5$ derivatives either in an appropriate solvent or in an evacuated tube without the solvent, or through the use of Strohmeier's method [8].

II. The CO stretching frequencies of $LCr(CO)_5$ derivatives

The spectra were assigned using well-established methods. The results are summarized in Table 2.

The spectra of these compounds in the CO stretching region exhibit two characteristics: (a) activation of the IR-forbidden B_1 mode in all compounds, and (b) separation of the $A_1(1)$ and E modes in the $(XC_6H_4)_3E$ substituted dervatives.

Several reasons for the activation of IR-forbidden CO fundamentals have been advanced by Bigorgne [9]. In many instances (e.g. PCl_2R, $PR'P_2$), activation is due to the presence of unsymmetrical ligands; this causes a lowering of the C_{4v} symmetry in the $LM(CO)_5$ molecule and a consequent splitting of the E mode. However, in the compounds studied here such a splitting has not been observed and thus activation of the B_1 mode could be due to the internal asymmetry of the ligands resulting in (*i*) a different degree of interaction of the phenylgroups with the C—O vibrators and (*ii*) activation of the transverse dipole moment vector as established by Keeling [10] in $XMn(CO)_5$ compounds. In this regard it should be noted that the same ligands also give rise to an abnormally large activation of the IR-forbidden A_{1g} and B_{1g} fundamentals in *trans*-$L_2Cr(CO)_4$ complexes [11].

The separation of the $A_1(1)$ and E modes for substituted chromium pentacarbonyl derivatives $(XC_6H_4)_3M$ may either be due to an intensity gain or to a frequency shift of the $A_1(1)$ mode, since we have found that these modes are unresolved in $LMo(CO)_5$ and $LW(CO)_5$ compounds [11], where L are the above-mentioned ligands.

As the $A_1(2)$ mode is more sensitive to M—L π-bonding variations and the intensity of the $A_1(2)$ frequency remains unchanged in the series $LCr(CO)_5$, $LMo(CO)_5$ and $LW(CO)_5$ the suggested increase in the intensity of the less

TABLE 2

L in $LCr(CO)_5$	$A_1(2)$	$A_1(1)$	B_1	E
$(C_6H_5)_3P$	2062.7	1942.3	1981.2	1942.3
$(4\text{-}FC_6H_4)_3P$	2064.3	1952.4	1982.7	1943.7
$(3\text{-}FC_6H_4)_3P$	2065.8	1954.4	1985.0	1945.6
$(4\text{-}ClC_6H_4)_3P$	2064.9	1953.8	1984.0	1945.0
$(3\text{-}ClC_6H_4)_3P$	2065.9	1955.3	1985.0	1946.7
$(C_6H_5)_3As$	2064.2	1944.5	1982.2	1944.5
$(4\text{-}FC_6H_4)_3As$	2065.6	1951.6	1983.9	1945.8
$(3\text{-}FC_6H_4)_3As$	2066.7	1947.4	1985.6	1947.4
$(4\text{-}ClC_6H_4)_3As$	2066.0	1951.5	1984.6	1946.3
$(3\text{-}ClC_6H_4)_3As$	2066.8	1952.5	1986.2	1947.8
$(C_6H_5)_3Sb$	2061.5	1944.7	1981.6	1944.7
$(4\text{-}FC_6H_4)_3Sb$	2063.1	1955.3	1984.0	1946.7
$(3\text{-}FC_6H_4)_3Sb$	2064.3	1956.9	1985.2	1948.4
$(4\text{-}ClC_6H_4)_3Sb$	2063.4	1956.1	1983.0	1947.5
$(3\text{-}ClC_6H_4)_3Sb$	2064.4	1957.4	1985.2	1949.3

sensitive $A_1(1)$ mode does not seem realistic. Hence, separation of the $A_1(1)$ and E modes is probably due to a frequency shift of the $A_1(1)$ mode to higher frequencies which occurs in the sequence $LCr(CO)_5 > LMo(CO)_5 > LW(CO)_5$ and may result from a corresponding π-donor sequence in the metal carbonyl portion of the molecule i.e. $\{W(CO)_5\} > \{Mo(CO)_5\} > \{Cr(CO)_5\}$.

III. MCO deformations and MC stretching vibrations

The wave numbers for the δ(M—C—O) and ν(M—C) vibrations occur in the range 700—300 cm^{-1} and according to Adams [12] the former normally occur at higher frequencies (and are more intense in the IR spectrum) than the latter which usually cover a narrower frequency range below 500 cm^{-1}. The wave numbers of the absorptions in these regions are given in Table 1. The number and types of infrared-active bands expected for $LM(CO)_5$ compounds, calculated using simple group techniques and based on the assumption that the substituents behave as point masses as far as the symmetry of the molecule as a whole is concerned, are $A_1 + 3E$ and $2A_1 + E$ for δ(M—C—O) and ν(M—C) respectively. For such complex and asymmetric compounds, however it should be pointed out that labelling bands as pure δ(MCO) or ν (MC) is likely to be inaccurate since all these vibrators are mixed to some extent. Nevertheless a particular absorption may be considered to be mainly δ(MCO) or ν(MC).

Since the tertiary aryl Group VB derivatives do not absorb strongly in the 600 cm^{-1} region, the δ(MCO) peaks are readily recognized and a comparison of the observed spectra with those of the free ligands [13] yields the δ(MCO) vibrations summarized in Table 1. However, only three bands are observed in the 700 — 500 cm^{-1} region of the spectrum although the fourth absorption may be hidden in the intense absorption due to the ligands (which occurs in the 500—520 cm^{-1} region). A further series of bands is also observed in the range 500—350 cm^{-1}.

Spectra in this region are however more complex due to the presence of bands associated with the ligands. In general, the lack of frequencies, the difficulty of assignment and the difficulty of knowing the extent to which the δ(MCO) and ν(MC) vibrations are mixed make it impossible to draw meaningful conclusions regarding this series of $LCr(CO)_5$ complexes.

TABLE 3

ASSIGNMENT OF CO FREQUENCIES FOR $LCr(CO)_4$ (^{13}CO) MOLECULES

L in $LCr(CO)_5$	Equatorial ^{13}CO		Axial ^{13}CO
	$A'\{A_1(2)\}$	$A'(E)$	$A_1(1)$
$(C_6H_5)_3P$	2055.2		
$(4\text{-}FC_6H_4)_3P$	2057.0	1911.7	
$(3\text{-}FC_6H_4)_3P$	2058.0	1914.3	1901.4
$(4\text{-}ClC_6H_4)_3P$	2057.4	1913.0	1899.2
$(3\text{-}ClC_6H_4)_3P$	2058.5	1914.0	1905.2
$(C_6H_5)_3As$	2056.4	1915.5	1903.9
$(4\text{-}FC_6H_4)_3As$	2058.5	1908.0	1897.0
$(3\text{-}FC_6H_4)_3As$	2059.3		
$(4\text{-}ClC_6H_4)_3As$	2058.2	1912.0	
$(3\text{-}ClC_6H_4)_3As$	2058.9		
$(C_6H_5)_3Sb$	2054.0	1915.6	1889.0
$(4\text{-}FC_6H_4)_3Sb$	2057.0	1913.6	
$(3\text{-}FC_6H_4)_3Sb$		1916.8	
$(4\text{-}ClC_6H_4)_3Sb$	2056.0	1916.5	
$(3\text{-}ClC_6H_4)_3Sb$	2057.0	1917.0	

IV. ^{13}CO stretching vibrations

Comparison with earlier data [14] enable the weak peaks attributable to $LCr(CO)_4$ (^{13}CO) molecules to be measured and assigned. The results are summarized in Table 3.

V. CO frequencies and bonding in $LCr(CO)_5$ compounds

The occurrence of π bonding between metals and phosphorus ligands is now widely accepted despite the fact that recently this subject has become rather controversial [15,16]. In studies of bonding by spectroscopy, compounds of the type $LM(CO)_5$, where L is generally a phosphine ligand, have been of particular interest. Although there are numerous IR data relevant to this subject, little attempt has been made to compare data for compounds where M is the same transition metal and where the ligands are related phosphines, arsines and stibines.

Such a comparison between the CO frequency shifts and the bonding is made here. Although the differences in frequencies are quite small, a general trend is observed for the characteristic $A_1(2)$ [$\nu^*(CO)$] fundamental, i.e. (1) $3\text{-}ClC_6H_4 \geqslant 3\text{-}FC_6H_4 > 4\text{-}ClC_6H_4 > 4\text{-}FC_6H_4 > C_6H_5$ and (2) $As > P > Sb$ both for the groups R and the atoms E in $R_3ECr(CO)_5$ respectively.

Correlation of $\nu^*(CO)$ and σ bonding a measure of which is given by the Hammett σ parameters in Table 4, yields the following sequence for the σ-donor capacity of the ligands: (3) $C_6H_5 > 4\text{-}FC_6H_4 > 4\text{-}ClC_6H_4 > 3\text{-}FC_6H_4 \geqslant 3\text{-}ClC_6H_4$ in complete agreement with the sequence found in related $LNi(CO)_3$ derivatives [17] in which $L \leftarrow Ni$ π bonding could be neglected. However the observed σ-donor capacity $Sb > P > As$ is opposite to the sequence $P > As > Sb$ found for $LNi(CO)_3$ compounds [17].

Correlation of $\nu^*(CO)$ and π bonding results in a sequence for the π-acceptor capacity of the ligands in complete agreement with sequence (1) above and in complete contrast both with the σ-donor capacity of the ligands in

TABLE 4

CORRELATION OF HAMMETT PARAMETERS AND σ BONDING

R	$\Sigma\sigma$	$A_1(2)$ (cm^{-1})		
		$R_3PCr(CO)_5$	$R_3AsCr(CO)_5$	$R_3SbCr(CO)_5$
C_6H_5	0.000	2062.7	2064.2	2061.5
$4\text{-}FC_6H_4$	0.186	2064.3	2065.6	2063.1
$4\text{-}ClC_6H_4$	0.681	2064.9	2066.0	2063.4
$3\text{-}FC_6H_4$	1.011	2065.9	2066.7	2064.3
$3\text{-}ClC_6H_4$	1.119	2065.9	2066.8	2064.4

$LNi(CO)_3$ (sequence (3) above) and with the synergic character of the M—L bond in the various metal carbonyls.

Hence it must be concluded that (a) tertiary aryl substituted Group VB derivatives generally act as σ-bonding ligands, although weak π bonding occurs, and (b) correlations between the characteristic CO frequency and the σ- or π-bonding capacities of the ligands as undertaken in the past are not particularly meaningful. More attention will be drawn to this subject in a following paper [17].

Acknowledgements

The authors wish to thank Mr. A. Bossuyt and Mr. R. Mouton for the synthesis of some compounds and Mr. F. Persyn for recording the IR spectra.

References

1 F.T. Delbeke, G.P. Van der Kelen and Z. Eeckhaut, J. Organometal. Chem., 16 (1969) 512.
2 F.T. Delbeke and G.P. Van der Kelen, J. Organometal. Chem., 21 (1970) 155.
3 T.A. Magee, C.N. Matthews, T.S. Wang and J.M. Wotiz, J. Amer. Chem. Soc., 83 (1961) 3200.
4 S.O. Grim and D.A. Wheatland, Inorg. Chem., 8 (1969) 1716.
5 R.F. De Ketelaere, E. Muylle, W. Vanermen, E. Claeys and G.P. Van der Kelen, Bull. Soc. Chim. Belges, 78 (1969) 219.
6 R.F. De Ketelaere, F.T. Delbeke and G.P. Van der Kelen. J. Organometal. Chem., 28 (1971) 217.
7 R.F. De Ketelaere, F.T. Delbeke and G.P. Van der Kelen, J. Oranometal. Chem., 30 (1971) 365.
8 W. Strohmeier and F.J. Muller, Chem. Ber., 102 (1969) 3608.
9 M. Bigorgne, R. Poilblanc and M. Pankowski, Spectrochim. Acta, A, 26 (1970) 1217.
10 G. Keeling, S.F.A. Kettle and I. Paul, J. Chem. Soc. (A), 1971) 3143.
11 F.T. Delbeke, Ph. D. Thesis.
12 D.M. Adams, J. Chem. Soc., (1964) 1771
13 F.T. Delbeke, R.F. De Ketelaere and G.P. Van der Kelen, J. Organometal. Chem., 28 (1971) 225.
14 F.A. Cotton, A. Musco and G. Yagupsky, Inorg. Chem., 6 (1967) 1357.
15 R.J.Angelici and M.D. Malone, Inorg. Chem.. 6 (1967) 1731.
16 L.M. Venanzi, Chem. Brit., (1968) 162.
17 F.T. Delbeke, to be published.