Journal of Organometallic Chemistry, 94 (1975) 181—188

EFFECT OF THE BRIDGING LIGANDS ON THE C—O STRETCHING FORCE CONSTANTS OF THE COMPOUNDS $Co_2(CO)_6(\mu\text{-}Y)_2$ AND $Fe_2(CO)_6(\mu\text{-}X)_2$ (WHERE Y = CO, P, As, CR AND X = S, SR, Se, PRR′, Br, I)*

GYÖRGY BOR

*C.N.R. Laboratory for the Chemistry of Radioelements, University of Padua (Italy) and Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology, ETH**, Zürich (Switzerland)*

For more than 10 years we have systematically collected infrared spectroscopic data for the group of binuclear cobalt and iron carbonyl derivatives which have a structure analogous to the one of the bridged form of $Co_2(CO)_8$ [1]. Our aims were:

(*a*) to identify an unequivocal and generally valid assignment for the C—O stretching modes of these compounds of idealized C_{2v} symmetry;

(*b*) to calculate the C—O stretching force and interaction constants for a considerable number of compounds of this structural class; and

(*c*) to reveal the effect of the μ_2-bridging ligands on the force constants.

Partial data on the spectral characteristics of some representatives of this class have been published earlier [2-8].

Spectra and assignment

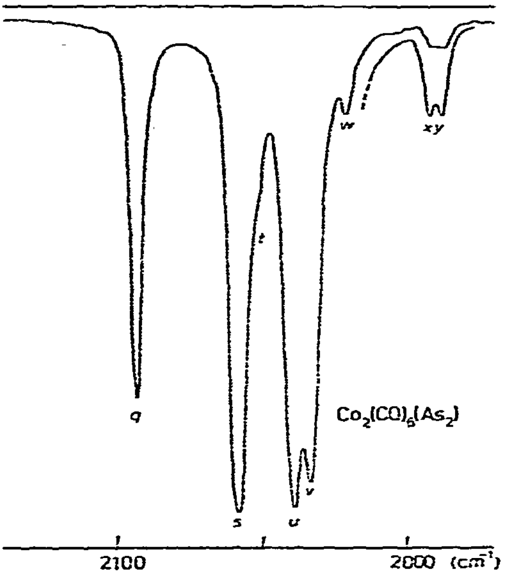
We have obtained the high-resolution spectra (spectral slit width: 0.8-1.2 cm^{-1}) for a number of these compounds prepared in part by other authors, but previously reported without good quality spectra. Our spectra of $Co_2(CO)_6(As_2)$ [9], $Fe_2(CO)_6(Se_2)$ [10], $Fe_2(CO)_6(PHCy)_2$ [11] (Cy = cyclohexyl), and $Fe_2(CO)_6Br_2$ [12] are shown, as examples in Figs. 1-4.

On the basis of calculations and, in part, ^{13}CO enrichment studies, the positions and assignment of the five IR active frequencies ($2A_1 + 2B_1 + B_2$) and of the one IR inactive (A_2) mode of the all-^{12}CO molecules, as well as the natural ^{13}CO-satellites were unequivocally established. The scheme for a "theoretical" spectrum is shown in Fig. 5. One ambiguity cannot be solved a priori: the often very small separation between bands *u* and *v* does not allow their uniform assign-

---

* Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.

** Present address.



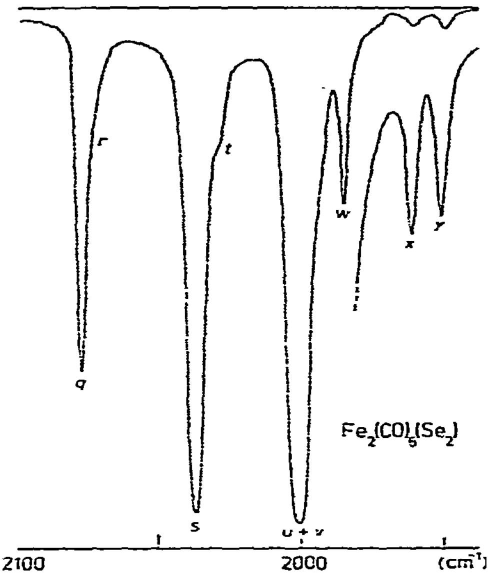


Fig. 1. Infrared spectrum of $Co_2(CO)_6(As_2)$ in the carbonyl stretching region (hexane solution).

Fig. 2. Infrared spectrum of $Fe_2(CO)_6(Se_2)$ in the carbonyl stretching region (hexane solution).

ment to $\nu_2(A_1)$ and $\nu_6(B_2)$, and the decision between "assignment I" ($\nu_2 > \nu_6$) and "assignment II" ($\nu_2 < \nu_6$) had to be found for each instance separately.

The assignments of the C—O stretching frequencies for the compounds studied are summarized in Table 1. As we see from Figs. 1-4 and from the data

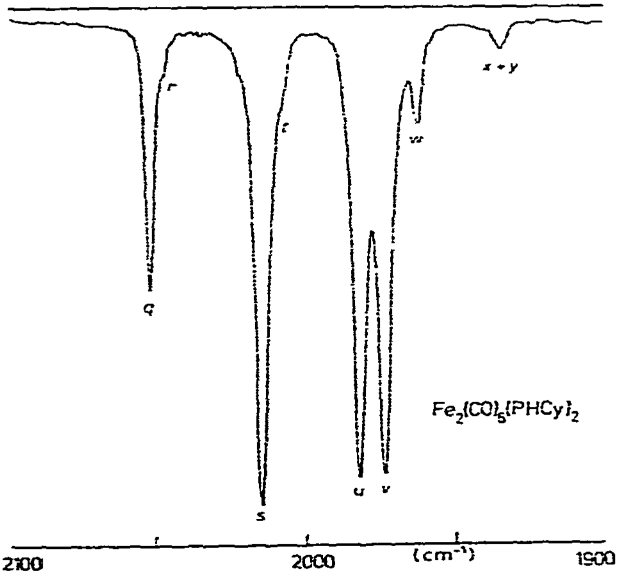
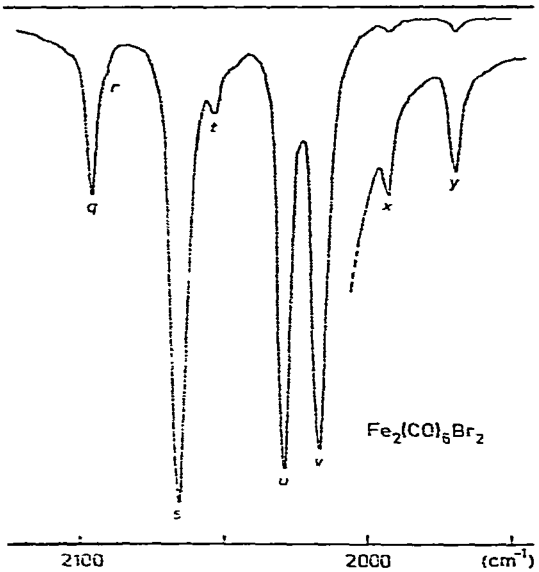


Fig. 3. Infrared spectrum of $Fe_2(CO)_6(PHC_6H_{11})_2$ in the carbonyl stretching region (hexane solution).



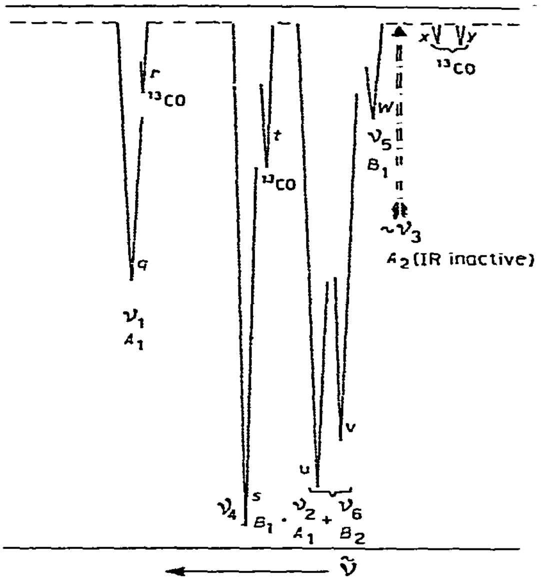


Fig. 4. Infrared spectrum of $Fe_2(CO)_6Br_2$ in the carbonyl stretching region (hexane solution).

Fig. 5. Schematic representation of an idealized spectrum of $M_2(CO)_6(\mu\text{-}X_2)$ compounds in the carbonyl stretching region.

in Table 1 not all the compounds show the clear-cut form of the spectrum shown schematically in Fig. 5. The apparent deviations can be discussed in the following groups:

(*1*) Bands ν_2 and ν_6 completely overlap ($Fe_2(CO)_6S_2$ and $Fe_2(CO)_6Se_2$) and the broader form of a bond composed of $u + v$ indicates a "hidden" separation by only 1.0-1.5 cm^{-1} (Fig. 2).

(*2*) The lowest and always weak all-^{12}C—O fundamental, w, is only slightly separated from its strong high-energy neighbour (ν_2 or ν_6), and hence it is completely hidden in the low frequency wing of the strong band. In these cases the ν_5 frequency was successfully calculated from the isotopic satellites x and y ($Fe_2(CO)_6X_2$, where X = Br or I, Fig. 4). In the case of the alkylthio bridged complexes of iron, $Fe_2(CO)_6(SR)_2$, the calculated ν_5 band was also observed at the calculated position in spectra taken on solutions of high concentrations (Fig. 6). (In previous papers only four [5, 13], or even only three [14] bands have been reported for these compounds.)

(*3*) The ^{13}C—O satellite t is merged into its parent band ν_4 (s) and can be observed only as a weak shoulder (Figs. 1,3).

(*4*) The two low-frequency isotopic satellites, always well separated from the main "body" of the spectrum, overlap each other. The broadening of the single observed band suggests a hidden separation of 1.0-2.0 cm^{-1} (Fig. 3).

(*5*) Complications arise from the presence of two (or more) inseparable isomers. The case of $Co_2(CO)_8$ has been the subject of a decade-long study and was resolved by isotopic enrichment experiments [8]. The assignment to one isomer of the two, out of the four weak low-frequency bands in the spectrum of $Fe_2(CO)_6(SC_6F_5)_2$ (cf. Fig. 8 in Ref. 6), is not straightforward. The combination

TABLE 1

ASSIGNMENT OF THE C—O STRETCHING FREQUENCIES OF SOME $(\mu\text{-X})_2M_2(CO)_6$ COMPOUNDS OF Co AND Fe[f]

	$\nu_1(A_1)$	$\nu_4(B_1)$	$\nu_2(A_1)$	$\nu_6(B_2)$	$\nu_5(B_1)$	$\nu_3(A_2)^a$ inactive	Lower ^{13}C—O satellites	
							ax	eq
$Co_2(CO)_8$ (bridged form)	2111.8	2071.0	2042.4	2044.0	2034.8^b	2021.5	2001.7	1994.0^c
$Co_2(CO)_6(P_2)$	2100.6	2066.3	2041.5	2045.5	2028.5	2026.0	1999.5	1994.2
$Co_2(CO)_6(HC_2H)$	2098.6	2058.8	2028.2	2034.0	2016.7	2014.0	1986.0	1984.0
$Co_2(CO)_6(HC_2CH_2OH)$	2097.5	2057.9	2026.2	2034.7	2016.0	2010.0	1982-1984	
$Co_2(CO)_6(HC_2C_6H_5)$	2094.5	2057.4	2027.7	2032.0	2016.0	2012.0	1983-1985	
$Co_2(CO)_6(As_2)$	2093.5	2058.0	2034.0	2039.0	2021.0	2019.0	1991.5	1987.5
$Co_2(CO)_6(C_6H_5C_2C_6H_5)$	2090.6	2056.0	2026.9	2030.4	2012.5	2005.0	1984.0	1977.0
$Co_2(CO)_6(CH_3C_2CH_3)$	2089.0	2047.5	2014.8	2025.0	2004.0	2003.0	1973	
$Fe_2(CO)_6Br_2$	2096.5	2066.0	2029.5	2017.0	(2013.5)^d	1999.0	1993.0	1970.0
$Fe_2(CO)_6(SC_6F_5)_2$	2089.5	2061.0	2026.0	2012.5	2006.5	2005.5	1987.5	1970.0
$Fe_2(CO)_6I_2$	2086.0	2055.5	2021.0	2011.0	(2006.0)^d	1991.5?	1983.2	1963.2
$Fe_2(CO)_6(S_2)$	2083.5	2043.5	2007^c	2006^e	1991.0	1984.5	1966.0	1956.0
$Fe_2(CO)_6(Se_2)$	2077.5	2037.0	2001^e	2000^e	1985.5	1978.0	1960.5	1950.0
$Fe_2(CO)_6(SCH_3)_2$-*anti*	2073.7	2037.5	2002.9	1992.4	1980.5	1971.8	1957.7	1944.6
$Fe_2(CO)_6(SCH_3)_2$-*syn*	2070.3	2037.9	1997.9	1990.2	1982.0	1973.2	1960.9	1943.7
$Fe_2(CO)_6(PHMe)_2$	2060.3	2022.7	1981.7	1990.6	1970.3	1973.4	1942.1	
$Fe_2(CO)_6(PHCy)_2$	2055.6	2018.2	1976.9	1985.4	1965.6	1970.2	1937.6	
$Fe_2(CO)_6(PMePh)_2$	2052.9	2014.7	1986.7	1968.7	1959.2		1938.1	1926.4
$Fe_2(CO)_6(PMe_2)_2$	2051.1	2013.2	1982.0	1968.0	1958.9	1953	1935.9	1926.9

[a] The IR inactive A_2 frequencies were calculated from the isotopic satellites. [b] Calculated value: overlapped by strong bands of the non-bridged form. [c] Observable only after ^{13}CO enrichment. [d] Calculated values, not observed due to the small separation from the strong B_2 band. [e] Broad, non resolved doublet. Values of limited accuracy. All values refer to hexane solutions. [f] Me = CH_3, Ph = C_6H_5, Cy = cyclo-C_6H_{11}.

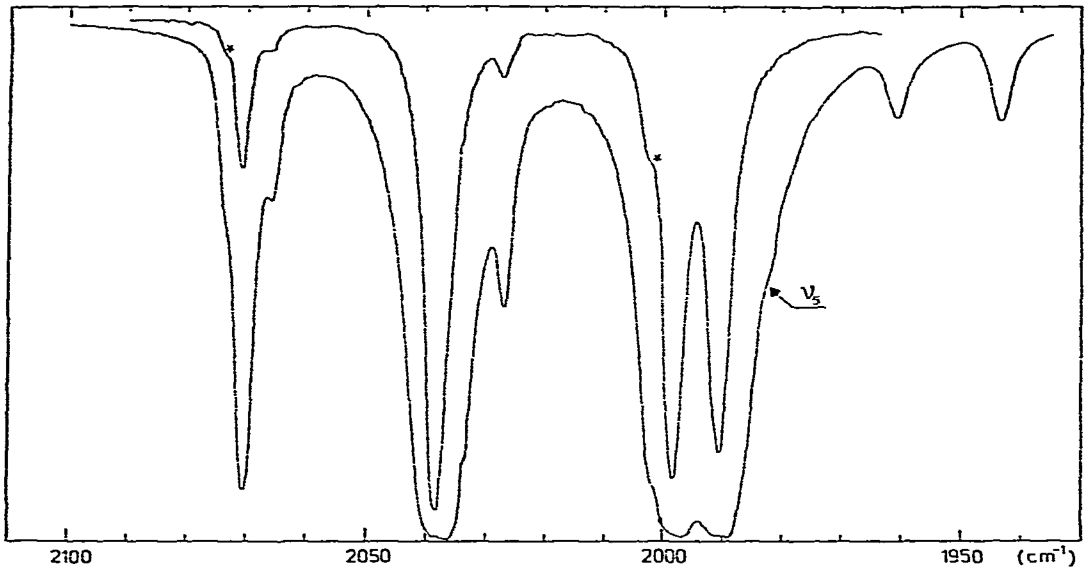


Fig. 6. Infrared spectrum of *syn*-$Fe_2(CO)_6(SCH_3)_2$ in the carbonyl stretching region; two concentrations (hexane solution). Shoulders belonging to the *anti* isomer formed during the scanning are labelled with asterisks.

chosen gave force and interaction constants in the best agreement with those of the other compounds.

Hence all spectra can be considered as belonging to the same five-band type with the characteristic intensity distribution shown by the "regular" spectra of e.g. $Co_2(CO)_6(As_2)$ (Fig. 1); deviations from this spectral type are only individual "distortions" by casual coincidences. Attempts to give theoretical explanations [13, 14] for a "necessarily" lower number of bands are, therefore, as underlined already at an earlier stage of these studies [15], fundamentally erroneous.

In the case of the *anti* isomers of the RS-bridged iron compounds, and also of the $Co_2(CO)_6(RC_2R')$ complexes with asymmetric acetylenic bridges, the molecular geometry is C_s rather than C_{2v}. In spite of this, the sixth band, demanded by this lower symmetry, was not observed for the alkylthio bridged iron compounds. For cobalt complexes with some asymmetric acetylenes (e.g. propyne), however, the very weak sixth band could be observed, at the frequency calculated for the A_2 mode of the C_{2v} model.

C—O Stretching force and interaction constants

Our parametric method [16] was used for the calculations. The extended application to dinuclear types demands the assumption, justified by previous successful applications, [17, 18] that the extent of local coupling between the different types of CO vibrators is equal for the two second order species. With this single constraint, one can calculate the two C—O stretching force constants, and the two geminal and four "remote" [i.e. M(CO) · · · M'(CO)] type inter-

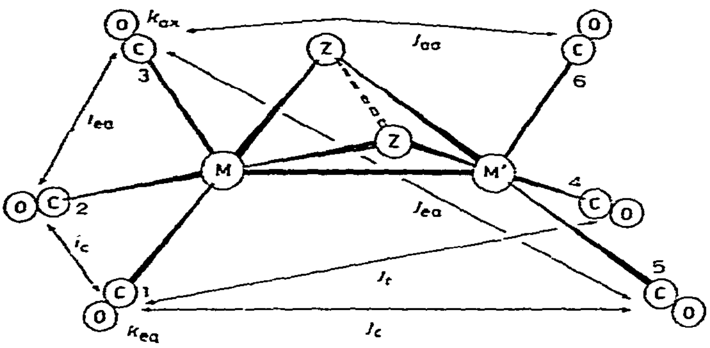


Fig. 7. Definition of the C—O stretching force and interaction constants.

action constants (defined as shown in Fig. 7) in a "factored C—O stretching force field". The results are given in Table 2.

Concerning the "remote" (or indirect) interaction constants we can see that:

(*i*) not even the "transoid" types (j_t, j_{ea}) are zero;

(*ii*) the two "cisoid" (j_c, j_{aa}) and the two "transoid" constants have similar, but not equal values.

These results prove that *it is equally* erroneous to neglect completely these CO ··· C'O' interactions as it is to assume for them a priori equal values [13], or to treat these spectra by supposing that only one, arbitrarily chosen remote interaction has a non-zero value [14]. A more complete force field cannot modify *qualitatively* these findings.

To visualize the relative influences of the bridging ligands on the *k*(CO)'s,

TABLE 2

C—O STRETCHING FORCE AND INTERACTION CONSTANTS (mdyn/Å)^a

	k_{eq}	k_{ax}	i_c	i_{ea}	j_t	j_c	j_{aa}	j_{ea}
$Co_2(CO)_8$	17.02	17.12	0.33	0.30	0.03	0.21	0.17	0.10
$Co_2(CO)_6(P_2)$	16.96	17.10	0.22	0.28	0.02	0.18	0.19	0.06
$Co_2(CO)_6(As_2)$	16.85	16.96	0.21	0.28	0.03	0.19	0.19	0.07
$Co_2(CO)_6(HC_2H)$	16.83	16.88	0.28	0.32	0.01	0.21	0.19	0.08
$Co_2(CO)_6(HC_2CH_2OH)$	16.82	16.84	0.30	0.32	0.02	0.22	0.17	0.08
$Co_2(CO)_6(HC_2Ph)$	16.80	16.86	0.26	0.31	0.04	0.20	0.18	0.08
$Co_2(CO)_6(PhC_2Ph)$	16.73	16.86	0.27	0.31	0.01	0.21	0.19	0.06
$Co_2(CO)_6(MeC_2Me)$	16.66	16.68	0.27	0.33	0.04	0.21	0.19	0.09
$Fe_2(CO)_6Br_2$	16.59	17.13	0.30	0.34	0.02	0.16	0.21	0.04
$Fe_2(CO)_6(SC_6F_5)_2$	16.55	17.05	0.24	0.33	0.07	0.12	0.21	0.03
$Fe_2(CO)_6I_2$	16.48	16.93	0.30	0.33	0.01	0.17	0.20	0.04
$Fe_2(CO)_6(S_2)$	16.39	16.65	0.31	0.37	0.03	0.21	0.23	0.07
$Fe_2(CO)_6(Se_2)$	16.29	16.55	0.31	0.37	0.03	0.21	0.23	0.08
$Fe_2(CO)_6(SMe)_2$-*syn*	16.16	16.61	0.29	0.37	0.03	0.16	0.21	0.05
$Fe_2(CO)_6(SMe)_2$-*anti*	16.22	16.54	0.35	0.37	0.04	0.20	0.24	0.04
$Fe_2(CO)_6(PHMe)_2$	16.13	16.22	0.26	0.37	0.04	0.18	0.18	0.08
$Fe_2(CO)_6(PHCy)_2$	16.07	16.14	0.26	0.37	0.05	0.17	0.18	0.08
$Fe_2(CO)_6(PMe_2)_2$	15.89	16.16	0.32	0.35	0.08	0.17	0.24	0.04

^{a} Me = CH_3, Ph = C_6H_5, Cy = cyclo-C_6H_{11}.

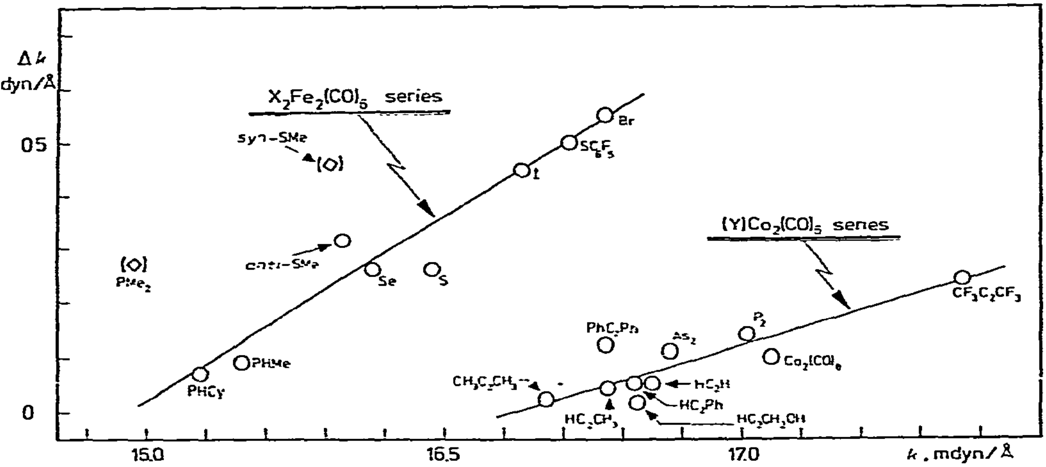


Fig. 8. $\Delta k = k_{ax} - k_{eq}$ *vs.* k(CO) plot. (The point of Y = $CF_3C_2CF_3$ has been added after the Symposium, and it is based on spectra through the courtesy of Prof. S.F.A. Kettle.)

we have plotted the differences $\Delta k = k_{ax} - k_{eq}$ vs. the average C—O stretching force constants, $\bar{k} = (k_{ax} + 2k_{eq})/3$ (Fig. 8). In each series we can notice that Δk increases linearly as $\bar{k}$ increases. Since $\bar{k}$ can be assumed to be a measure of the "net donation of electrons" from the bridging groups to the metal atoms, and Δk should be a measure of the π-bonding effect [19] of the bridging ligands, this trend observed for bridging hetero groups is analogous to that found for terminal ones [19-21].

The complexes $Fe_2(CO)_6(PMe_2)_2$ and *syn*-$Fe_2(CO)_6(SMe)_2$ do not follow the general trend but have anomalously high Δk values. The X-ray study of the former compound [22] indicated that there is a considerable interaction between the two methyl groups oriented toward each other.

In the case of the *syn*-methylthio compound MO calculations [23] showed that the two lone pairs on the sulpur atoms, oriented towards each other, may interact. These interactions, accompanied by small distortions of the $M_2(CO)_6$ skeleton, may significantly alter the single (σ and π) contributions, without affecting the "net charge donation".

The isotopic satellites of the PMePh-bridged compound defied satisfactory agreement with calculations proving that this compound cannot be treated on the basis of C_{2v} symmetry. A full account of this study will be published elsewhere.

Acknowledgements

The author thanks the late Professor Sir Ronald S. Nyholm (UCL) and Professor U. Croatto (Padua) for the excellent working facilities in the periods 1968/69 and 1969/73, respectively. Thanks are due to Prof. K. Issleib (Halle), Dr. A. Koerner von Gustorf (Mülheim/Ruhr), Prof. L.F. Dahl and Prof. P.M. Treichel (Madison, Wisconsin), Prof. S.F.A. Kettle (Norwich) and Dr. G. Pályi (Veszprém) for the kind donation of samples, and for the personal communication of unpublished structural or spectral data. The collaboration of Drs. G.

Natile (Venice) and F. Marcati (Padua) in the preparation of some complexes and assistance with the calculations [7] is gratefully acknowledged.

References

1 G.G. Summer, H.P. Klug and L.E. Alexander, Acta Cryst., 17 (1964) 732.
2 G. Bor, Spectrochim. Acta, 19 (1963) 2065.
3 G. Bor, Chem. Ber., 96 (1963) 2644.
4 G. Bor, Thesis of Habilitation for Cand. Sci. of the Hungarian Academy of Sciences, Budapest (1966).
5 G. Bor, J. Organometal. Chem., 11 (1968) 195.
6 L. Maresca, F. Greggio, G. Sbrignadello and G. Bor, Inorg. Chim. Acta, 5 (1971) 667.
7 F. Marcati, Thesis of Laurea, Univ. of Padua (1971).
8 G. Bor and K. Noack, J. Organometal. Chem., 64 (1974) 367.
9 A.S. Foust, M.S. Foster and L.F. Dahl, J. Amer. Chem. Soc., 91 (1969) 5633.
10 W. Hieber and W. Beck, Z. Anorg. Allg. Chem., 305 (1960) 265.
11 K. Issleib, personal communication (1955).
12 E. Koerner von Gustorf, J.C. Hogan and R. Wagner, Z. Naturforsch. B, 27 (1972) 140.
13 E. Kostiner, M.L.N. Reddy, D.S. Urch and A.G. Massey, J. Organometal. Chem., 15 (1968) 383; M.L.N. Reddy and D.S. Urch, Discuss. Faraday Soc., 47 (1969) 53.
14 R.E. Dessy and L. Wieczorek, J. Amer. Chem. Soc., 91 (1969) 4963.
15 G. Bor, Discuss. Faraday Soc., 47 (1969) 65.
16 G. Bor, Inorg. Chim. Acta, 1 (1967) 81.
17 G. Bor, Inorg. Chim. Acta, 3 (1969) 169.
18 G. Bor and G. Sbrignadello, J. Chem. Soc. Dalton, (1974) 440.
19 W.A.G. Graham, Inorg. Chem., 7 (1968) 315 and refs. therein.
20 R.F. Fenske, Pure Appl. Chem., 27 (1971) 61; M.B. Hall and R.F. Fenske, Inorg. Chem., 11 (1972) 768, 1619.
21 R.A. Brown and G.R. Dobson, Inorg. Chim. Acta, 6 (1972) 65.
22 J.R. Huntsman, Ph.D. Thesis, University of Wisconsin, Madison (1973).
23 B.K. Teo, Ph.D. Thesis, University of Wisconsin, Madison (1973).