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SPECTROSCOPIC STUDIES AND REACTIONS OF $Cp_2Ni_2RC_2R'$ COMPLEXES

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Summary

Some new complexes in the series $Cp_2Ni_2RC_2R'$ (Cp = π-cyclopentadienyl; R = H, R' = CH_3; R = CH_3, R' = C_6H_5; R = R' = $COOCH_3$) have been synthesized and the effect of the R and R' groups in the displacement $Cp_2Ni_2RC_2R' + R''C_2R''' \rightleftharpoons Cp_2Ni_2R''C_2R''' + RC_2R'$ has been investigated. Spectroscopic properties (IR, ^1H and ^{13}C NMR) are described, the nature of the bond between acetylene and nickel is discussed and it is suggested that the triple bond of the coordinated acetylene has virtually total olefinic character.

Introduction

Transition metal acetylene complexes, in which the acetylene ligand retains its identity, may be classified as mononuclear and binuclear (or polynuclear) complexes, depending upon whether the ligand is coordinated to one metal atom or acts as a bridging group between two (or more) metal centres. Mononuclear complexes of several metals have been widely studied [1], in particular, the properties of the metal—alkyne bond have been investigated by means of IR [2] and NMR [3] spectroscopic analysis, and rate [4] and equilibrium [5] studies of the acetylene displacements have been made.

Compounds with bidentate bimetallic alkyne ligands, on the contrary, have been scarcely investigated, the few reported data referring to the alkyne derivatives of dicobalt octacarbonyl $Co_2(CO)_6RC_2R'$ and of dirhodium octa(trifluorophosphine) $Rh_2(PF_3)_6RC_2R'$, in which the acetylene RC_2R' acts as a bidentate bridging ligand between the two symmetric $Co(CO)_3$ and $Rh(PF_3)_3$ moieties, respectively. Qualitative [6] and semiquantitative [7] observations on the ligand displacement and a spectroscopic study [8] of the structure and bonding of the alkyne in $Co_2(CO)_6RC_2R'$ complexes have been reported. More recently a preliminary investigation on X-ray and spectroscopic properties of the rhodium derivatives has appeared [9].

On the other hand complexes of general formula $Cp_2Ni_2RC_2R'$ obtained from the reaction of $(NiCpCO)_2$ [10] or $NiCp_2$ [11] with acetylenes, are known to be entirely analogous to the acetylene cobalt complexes on the basis of X-ray diffraction studies [12]. We therefore considered it interesting to examine in detail a number of $Cp_2Ni_2RC_2R'$ complexes, and we report below the results of spectroscopic (IR, ^1H and ^{13}C NMR) investigations and of observations on the alkyne displacement, with particular reference to the nature of the R and R' groups.

Experimental

Compounds and solvents

Bis(cyclopentadienylnickel carbonyl) (Alfa Inorganics) was crystallized from n-heptane at −20° and stored under nitrogen. Diphenylacetylene (Fluka AG), phenylacetylene (Fluka AG), 2-butyne (K and K), dimethylacetylene dicarboxylate (Aldrich), acetylene, propyne (K and K) and hexafluoro-2-butyne (K and K) were commercial products. Solids were recrystallized from n-heptane; liquids were distilled under reduced pressure; gases were collected in a cold trap. 1-Phenylpropyne was prepared by dehydrochlorination of a mixture of 2-chloro-1-(or -3-)phenylpropene, according to the published method [13].

Solvents (reagent grade) were purified and dried by standard methods.

The synthesis of some $Cp_2Ni_2RC_2R'$ complexes has been previously reported: $Cp_2Ni_2C_6H_5C_2C_6H_5$ [10]: $Cp_2Ni_2HC_2C_6H_5$ [10], $Cp_2Ni_2CH_3C_2CH_3$ [10]; $Cp_2Ni_2HC_2H$ [10, 11]; $Cp_2Ni_2CF_3C_2CF_3$ [14]. Differences in the isolation and characterization procedures from those given in refs. 10 and 11 are mentioned below.

$Cp_2Ni_2HC_2CH_3$

$Cp_2Ni_2(CO)_2$ (2.31 g, 7.6 mmole) and toluene (300 ml) were placed in a 500 ml pressure glass vial, cooled with liquid nitrogen, and degassed. About 0.8 g of propyne (ca. 20 mmole) were then introduced, and the vial was sealed and kept at 110° for 24 h. Solvent was removed at reduced pressure from the deep green solution, and the residue was dissolved in the minimum amount of n-heptane and filtered. The solution was chromatographed on alumina, with n-heptane as eluent, in a glovebox under an inert atmosphere. Unreacted $Cp_2Ni_2(CO)_2$ eluted first, followed by a very intense green band, which was collected, concentrated to 50 ml and crystallized at −20° under nitrogen to give $Cp_2Ni_2HC_2CH_3$ (1.42 g, ca. 65%) as deep green microcrystals, very soluble in common organic solvents. The complex is fairly stable as solid and decomposes rapidly in solution on exposure to air. (Found: C, 54.4; H, 5.0; Ni, 40.6; Mol.wt. 286 by mass spec. $C_{13}H_{14}Ni_2$ calcd.: C, 54.3; H, 4.9; N, 40.8%; Mol.wt. 287.7).

$Cp_2Ni_2HC_2H$

This compound was prepared and isolated in the manner described for $Cp_2Ni_2HC_2CH_3$. $Cp_2Ni_2(CO)_2$ (2.06 g, 6.8 mmole) and acetylene (0.5 g, ca.

20 mmole) yielded $Cp_2Ni_2HC_2H$ (1.27 g) (Found: C, 52.9; H, 4.5; Ni, 43.1; Mol.wt. 272 by mass spec. $C_{12}H_{12}Ni_2$ calcd.: C, 52.7; H, 4.4; Ni, 42.9%; Mol.wt. 273.7).

$Cp_2Ni_2CH_3C_2CH_3$

The reaction mixture obtained from $Cp_2Ni_2(CO)_2$ and 2-butyne in toluene was filtered and evaporated and the residue was chromatographed under nitrogen on an alumina column (eluent n-heptane), as described above. $Cp_2Ni_2CH_3C_2CH_3$ was obtained in good yield (ca. 60%) by crystallization at −20°. (Found: C, 55.9; H, 4.5; Ni, 39.1; Mol.wt. 300 by mass spec. $C_{14}H_{16}Ni_2$ calcd.: C, 55.7; H, 5.3; Ni, 38.9%; Mol.wt. 301.7).

$Cp_2Ni_2CH_3C_2C_6H_5$

$Cp_2Ni_2(CO)_2$ (3.25 g, 10.7 mmole) and 1-phenylpropyne (3.8 ml, ca. 30 mmole) were placed in a three-necked flask, with gas inlet, reflux and Hg valve, previously purged with N_2. The solution was refluxed for about a day, until it became dark green; then the mixture was filtered and the solvent removed. The residual oil, dissolved in n-heptane and chromatographed as described previously, yielded $Cp_2Ni_2CH_3C_2C_6H_5$ (2.72 g) as darkgreen needles, m.p. 108°. The complex is oxidized in air slowly in the solid state and quite rapidly in solution, so that it should be handled under nitrogen. (Found: C, 62.5; H, 5.1; Ni, 32.1; Mol.wt. 362 by mass spec. $C_{19}H_{18}Ni_2$ calcd.: C, 62.7; H, 5.0; Ni, 32.3%; Mol.wt. 363.8).

$Cp_2Ni_2COOCH_3C_2COOCH_3$

The preparation was carried out in the same manner used for the phenylpropyne complex. The residue, after removal of the solvent, was purified by thin layer chromatography (adsorbent: Silicagel G from Stahl; developer: 1/4 solution of ethyl ether/petroleum ether). Crystallization from n-heptane at −20° gave green crystals of the compound, m.p. 106°, in good yield (ca. 75%). (Found: C, 49.0; H, 4.3; Ni, 30.3; Mol.wt. 388 mass spec. $C_{16}H_{16}Ni_2O_4$calcd.: C, 49.3; H, 4.1; Ni, 30.1%; Mol.wt., 389.7).

Displacement reactions

The reactions were carried out in n-heptane solution under nitrogen at constant (± 0.1°) temperature, using ca. 2.0 mmole of complex and a 2 - 10 fold excess of ligand.

Glass vials, as illustrated previously [5], were used, fitted with a rubber serum cap, to permit withdrawal of aliquots from the reaction mixture by means of a microsyringe. In order to avoid introduction of air during the removal of samples, the vials were sealed under a slight positive pressure of nitrogen. The samples were analysed by TLC under nitrogen and compared with blank samples, chromatographed under the same conditions. In all cases Silicagel G was the adsorbent, and various ethyl ether/petroleum ether solutions were used as developers.

At the end of each reaction, the product was isolated by chromatography on alumina and characterized by IR, NMR and mass spectra.

With gaseous ligands (acetylene, propyne, hexafluoro-3-butyne) reactions were carried out in sealed glass vials, between 8 and 10 vials being used for each reaction. At suitable intervals the vials were opened and the contents analysed.

Apparatus

Infrared spectra were recorded on a Beckman IR 12 double beam spectrophotometer, with KBr discs. PMR spectra were obtained with a Varian HA 100 spectrometer as $CDCl_3$ solutions with TMS as internal standard; CMR spectra were obtained with a Bruker HFX-90 spectrometer as 80% $CDCl_3$, 15% C_6F_6, 5% TMS solutions. The samples were contained in sealed tubes under nitrogen.

Mass spectra were recorded with an Hitachi RMU-6H single focussing mass spectrometer.

Analyses for carbon and hydrogen were carried out with a Model 185 C, H and N analyser (F and M Scientific Co.); for nickel, a Perkin—Elmer Model 303 atomic absorption spectrophotometer with DCRl was used.

Melting points were recorded on a Leitz Model 350 heating plate.

Results

Infrared spectra

Detailed IR frequencies for $Cp_2Ni_2RC_2R'$ complexes, have not been reported hitherto. In order to achieve a tentative assignment of the main absorption band, comparison has been made with the spectra of $NiCp_2$ and $Cp_2Ni_2(CO)_2$, for which a fairly complete assignment of the absorption frequencies is available [15].

Some frequencies appear in all the spectra essentially at the same positions and with quite similar intensities. These are probably due to the vibrations within the cyclopentadiene rings, and appear to be almost independent of the nature of the acetylene ligand. Frequencies of great importance because of their intensity are the strong doublet near 800 cm^{-1} assigned to CpC—H out-of-plane bending vibrations; the weak absorption at 806 and 840 cm^{-1} and the medium absorption at 1050 cm^{-1} are probably due to the same bending mode. C—H in-plane bending vibrations of the Cp rings appear as a medium-strong doublet near 1000 cm^{-1}. The appearance of a sharp absorption at 1110 cm^{-1} suggests that it may be a ring breathing frequency (cf. $NiCp_2$ 1112 cm^{-1}), whereas the band near 1420 cm^{-1} may be due to the C=C stretching mode. The cyclopentadienyl C—H stretching modes appear as weak absorptions near 3100 and 2960 cm^{-1}. The appearance of a series of weak bands around 1700 cm^{-1} are interpreted as combination and overtone bands involving CH modes, as proposed for the spectra of ferrocene and ruthenocene [15a].

The R and R' group vibrations are assigned by comparison with the spectra of the free acetylene ligands: little change in frequency has been observed. Typical absorptions of the phenyl groups are: two strong bands at 690 and 757 cm^{-1} (C—H out-of-plane bending); a medium intensity doublet at 1028 and 1068 cm^{-1} (C—H in-plane bending); a series of medium intensity adsorptions between 1450 and 1600 cm^{-1} (C=C stretching and skeletal deformations) and of weak intensity absorptions between 3000 and 3100 cm^{-1} (C—H stretching). CH_3 modes occur near 1440 cm^{-1} (CH_3 bending) and at 2830 to 2970 cm^{-1} (C—H stretching). In Cp_2Ni_2 $COOCH_3C_2COOCH_3$ four

TABLE 1

^{1}H AND ^{13}C NMR SPECTRAL DATA[a]

Complex		^{1}H		^{13}C	
		$\delta(C_5H_5)$[b]	Other	$\delta(C_5H_5)$	Other
(I)	$Cp_2Ni_2CH_3C_2CH_3$	5.197 (s)	2.28[c] (s)	87.5	18.2[c]
(II)	$Cp_2Ni_2HC_2CH_3$	5.229 (s)	4.66[d,e] (q) 2.45[c,e] (d)	87.7	19.3[c]
(III)	$Cp_2Ni_2CH_3C_2C_6H_5$	5.219 (s)	8.55 (m), 8.23[f] (m); 2.51[c] (s)	87.8	130.6[g]; 128.6 127.3[i]; 19.2[c]
(IV)	$Cp_2Ni_2HC_2H$	5.214 (s)	4.95[d] (s)	87.4	
(V)	$Cp_2Ni_2HC_2C_6H_5$	5.281 (s)	8.52 (m), 8.22[f] (m); 5.11[d] (s)	88.1	131.5[g]; 128.7 127.8[i]
(VI)	$Cp_2Ni_2C_6H_5C_2C_6H_5$	5.299 (s)	8.55 (m), 8.27[f] (m)	88.3	130.7[g]; 128.7 127.6[i]
(VII)	$Cp_2Ni_2COOCH_3C_2COOCH_3$	5.414 (s)	3.78[j] (s)	88.9	53.2[j]
(VIII)	$Cp_2Ni_2CF_3C_2CF_3$	5.426 (s)		88.6	

[a] δ in ppm positive downfield from TMS internal reference; [b] Uncertainty ± 0.003 ppm; [c] $-CH_3$; [d] $\equiv CH$; [e] $\neq {}^4J(H-H) \approx 1.5$ Hz; [f] C_6H_5; [g] $C_{3,5}$ phenyl; [h] $C_{2,6}$ phenyl; [i] C_4 phenyl; [j] OCH_3.

strong absorptions also appear between 1050 and 1250 cm^{-1}, which are assigned to C—O—C stretching modes and there is also a very intense band at 1718 cm^{-1} (C=O stretching). Finally, the spectra of $Cp_2Ni_2CF_3C_2CF_3$ show the typical C—F absorptions at 693 and 731 cm^{-1} (CF_3 bending [16]) and at 1141, 1195 and 1278 cm^{-1} (C—F stretching).

NMR spectra

^{1}H and ^{13}C NMR spectral data are reported in Table 1, the main feature of the PMR spectra being the sharp singlet due to the cyclopentadienyl protons. Each aromatic region in III, V and VI shows two multiplets with an integrated ratio of 2/3. The methyl absorption of I and III is a singlet and of II a doublet. The acetylenic protons are observed in CS_2 solution as a quartet for II and as a singlet for IV, whereas V shows only the phenyl and cyclopentadienyl resonances. On the basis of the integration ratio and of the comparison between the shift of II and IV we conclude that there is an unfortunate superposition of the cyclopentadienyl signal and the acetylenic proton [*]. The methoxyl resonance of VII is in the usual range. Proton noise decoupled CMR spectra show the usual features.

Displacement reactions

One acetylene displaces another from its complex, indicating ready equilibration of the type:

$$Cp_2Ni_2RC_2R' + R''C_2R''' \rightleftharpoons Cp_2Ni_2R''C_2R''' + RC_2R'$$

This reaction proceeds easily at 70 - 80° in an inert solvent such as n-heptane, without detectable formation of side products. From qualitative observations of both complex concentrations, we have found that the equilibrium constants depend essentially on the nature of the R, R', R'' and R''' groups. The following sequence of ligand displacement has been established: $CF_3C_2CF_3 \gg$

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[*] In a trial with added pyridine we did not observe any separation of the two peaks.

$COOCH_3C_2COOCH_3 > C_6H_5C_2C_6H_5 > C_6H_5C_2H > HC_2H \geqslant C_6H_5C_2CH_3 > CH_3C_2H > CH_3C_2CH_3$, in which any ligand can be preferentially replaced by any foregoing one.

The reaction proceeds rapidly to completion when the entering ligand precedes the displaced one by two places or more (in the above sequence), even when only a small excess of ligand is used. When the effective equilibrium conditions are established, the order of reactivity is easily determined on the basis of the equilibrium shift.

Discussion

It is generally accepted that the bonding model suggested by Dewar [17] and Chatt and Duncanson [18] for metal—olefin complexes, holds for the metal—acetylene coordinate bond. This bond involves overlapping of the occupied orbital of the acetylene with a vacant metal orbital (σ-component) and of the vacant antibonding $\pi^\star$ orbital of the acetylene with an occupied metal orbital (π-component). Whether the σ- or π-component predominates will depend upon the energy levels of both metal and acetylene; when the metal atoms have the same oxidation number and the same ligand environment, as occurs in the series $Cp_2Ni_2RC_2R'$, the energy levels of the acetylene orbitals are the principle factor determining the stability of the metal-acetylene bond.

Calculations [19] show that electron withdrawing groups on the acetylene ligand lower than the antibonding $\pi^\star$ orbitals, so rendering the π-component of the bond more important. The displacements show that the stability of the complexes increases as the groups on the coordinated acetylene vary in the order: $CF_3 > COOCH_3 > C_6H_5 > H > CH_3$, i.e. in the same order as the electron withdrawing ability of the groups increases. If Taft's polar constants $\sigma^\star$ are taken as measure of the inductive effect [20], we have the following sequence: CF_3 2.9; $COOCH_3$ 2.0; C_6H_5 0.60; H 0.49; CH_3 0.00, which implies that the strength of the π bond from nickel to acetylene is more important than the σ bond from acetylene to nickel for the formation of stable Ni-acetylene bonds, if synergic considerations are avoided. This sequence is consistent with the differing reactivity of the acetylene derivatives towards $Cp_2Ni_2(CO)_2$ on the reaction leading to $Cp_2Ni_2RC_2R'$ complexes [21].

A considerable π-component in the metal acetylene bond should be indicated by IR and NMR spectral data, since a reduction in triple bond character and development of double bond character is expected: the triple bond IR stretching frequency is lowered [2] by ca. 500 cm^{-1} and the ≡CH proton resonance is shifted lowfield by 2 to 5 ppm [5]. We have been unable to detect the C≡C stretching frequency, because of the presence of many absorptions in the 1400 to 1700 cm^{-1} region, but there is nevertheless some spectroscopic evidence that the acetylene character of the ligand is reduced. In the IR spectra of II, IV and V there are no absorptions near 3300 cm^{-1}, typical of ≡C—H stretching modes [22]. It is probable that this absorption appears near 3000 cm^{-1}, i.e., in the region of an olefin hydrogen stretching vibration. The PMR spectra of the complexes show a large downfield shift for the ≡C—H resonance

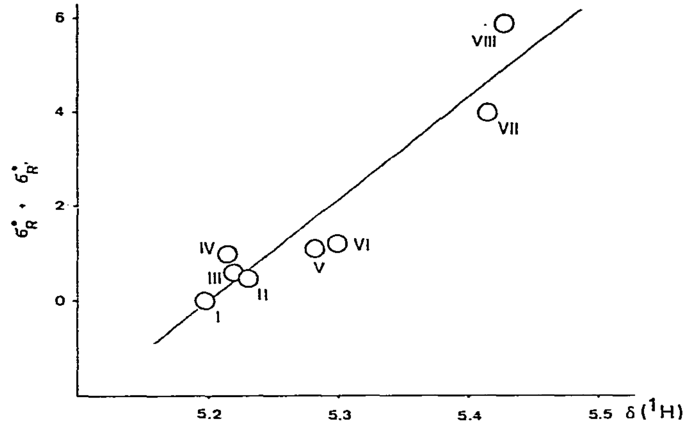

Fig. 1. Plots of the Taft's σ^* values of the R and R′ groups vs. $\delta(^1H)$ of the cyclopentadienyl ligands. Numbers are referred to Table 1.

compared with the free ligand spectra*. Moreover if we compare $|^4J(H—H)|$ for II with the observed values of propyne (−2.90 Hz) [23] and propene (*cis* −1.75 Hz; *trans* −1.33 Hz) [24], we see that $^4J(H—H)$, at least in magnitude, is very close to the propene long-range coupling constant. Both observations are consistent with the proposed hybridization change of the acetylenic carbon upon complexation.

One model of the metal—cyclopentadiene bond consists of a donor triple bond (from cyclopentadiene to metal), and some back-bonding, from metal to cyclopentadiene [25]. An increase of electron density on the metal atom should favour the back-bonding component, so raising the π-electron density of the C_5H_5 ring. This should increase the shielding and hence the chemical shift of both cyclopentadienyl protons and carbons. Figures 1 and 2 show plots of

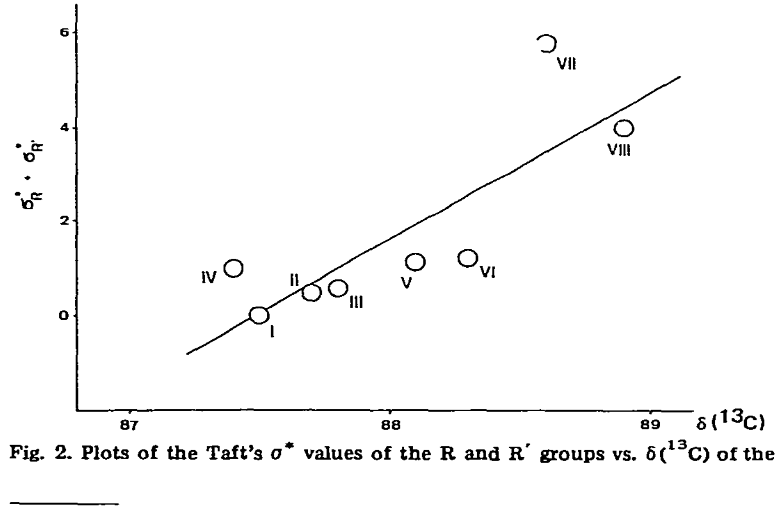

Fig. 2. Plots of the Taft's σ^* values of the R and R′ groups vs. $\delta(^{13}C)$ of the cyclopentadienyl ligands.

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[*] The $\delta(^1H)(\equiv H)$ for acetylene, methylacetylene and phenylacetylene are 1.80, 1.88 and 2.93, respectively.

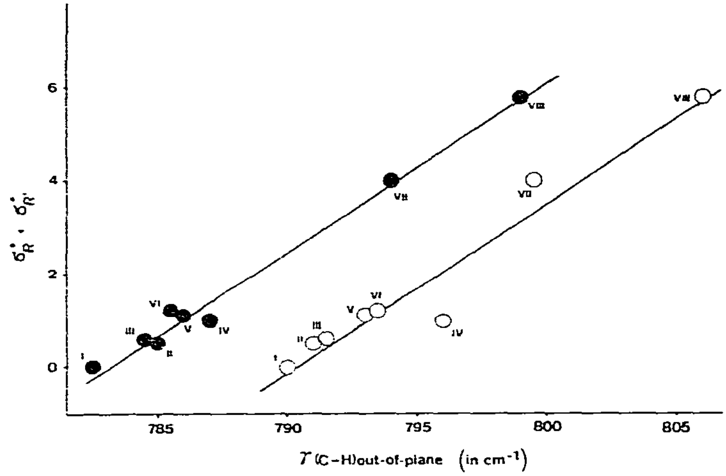

Fig. 3. Plots of the Taft's σ^* values of the R and R$'$ groups vs. the frequency values of the C—H out-of-plane bending vibration of the cyclopentadienyl ligands. Open circles and filled circles refer to the two values of the C—H bands.

$(\sigma^*_R + \sigma^*_{R'})$ vs. δ (^{1}H)(C_5H_5) and δ (^{13}C)(C_5H_5) for $Cp_2Ni_2RC_2R'$ complexes. The fairly good linear relationships indicate that the inductive effect of the groups bonded to the acetylene determines the electron density on the metal, and that this effect is transmitted to the cyclopentadiene groups via carbon—nickel bonds. Additionally it has been reported [26] that the values of the IR C—H out-of-plane bending vibrations in benzenoid systems are related to the π-electron density associated with the rings, so that as the electron density increases, the vibrations occur more easily and hence a relatively lower frequency results. Therefore, the C—H out-of-plane bending frequencies of the cyclopentadienyl ligands should correlate with the values of the Taft's constant for R and R$'$. This relation does give positive linear plots, as illustrated in Fig. 3, thereby confirming the previous conclusion drawn from the NMR relationships.

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References

1 F.L. Bowden and A.B.P. Lever, Organometal. Chem. Rev., 3 (1968) 227;
U. Belluco, B. Crociani, R. Pietropaolo and P. Uguagliati, Inorg. Chim. Acta Rev., 3 (1969) 19;
F.R. Hartley, Chem. Rev., 69 (1969) 799;
J.H. Nelson and J.B. Jonassen, Coord. Chem. Rev., 6 (1971) 27;
F.R. Hartley, Angew. Chem. Int. Ed. Engl., 11 (1972) 596.
2 J. Chatt, R.G. Guy, L.A. Duncanson and D.T. Thompson, J. Chem. Soc., (1963) 5170;
J.P. Collman and J.W. Kang, J. Amer. Chem. Soc., 89 (1967) 844.
3 C.D. Cook and K.Y. Wan, J. Amer. Chem. Soc., 92 (1970) 2595;
M.H. Chisolm, H.C. Clark, L.E. Manzer and J.B. Stothers, J. Amer. Chem. Soc., 94 (1972) 5087.
4 A.D. Allen and C.D. Cook, Can. J. Chem., 41 (1963) 1235;
A.D. Allen and C.D. Cook, Can. J. Chem., 42 (1964) 1063;
A.D. Allen and T. Theophanides, Can. J. Chem., 43 (1965) 290.
5 J. Chatt, B.L. Shaw and A.A. Williams, J. Chem. Soc., (1962) 3269;
J. Chatt, G.A. Rowe and A.A. Williams, Proc. Chem. Soc., (1967) 208.

6 G. Cetini, O. Gambino, R. Rossetti and E. Sappa, J. Organometal. Chem., 8 (1967) 149.
7 G. Cetini, O. Gambino, P.L. Stanghellini and R. Rossetti, Accad. Naz. dei XL 1967, Sez. IV, vol. XVIII, 89.
8 Y. Iwashita, F. Tamura and A. Nakamura, Inorg. Chem., 8 (1969) 1179;
Y. Iwashita, Inorg. Chem., 9 (1970) 1178;
Y. Iwashita, A. Ishikawa and M. Kainosho, Spectrochim. Acta, A, 27 (1971) 271.
9 M.A. Bennett, R.N. Johnson, G.B. Robertson, T.W. Turney and P.O. Whimp, J. Amer. Chem. Soc., 94 (1972) 6540.
10 J.F. Tilney-Bassett, J. Chem. Soc., (1961) 577.
11 M. Dubeck, J. Amer. Chem. Soc., 82 (1960) 502.
12 W.J. Sly, J. Amer. Chem. Soc., 81 (1959) 18;
O.S. Mills and B.W. Shaw, J. Organometal. Chem., 11 (1968) 595.
13 C.D. Hurt and A. Tockman, J. Org. Chem., 23 (1958) 1087.
14 J.L. Boston, D.W.A. Sharp and G. Wilkinson, J. Chem. Soc., (1962) 3488.
15 E.R. Lippincott and R.D. Nelson, Spectrochim. Acta, 10 (1958) 307;
H.P. Fritz, Chem. Ber., 92 (1959) 780;
H.P. Fritz, in F.G.A. Stone and R. West (Eds.), Advances in Organometallic Chemistry, Academic Press, New York, 1964, Vol. 1, p. 239.
16 E.E. Ferguson, L. Mikkelen, J.R. Nielsen and D.C. Smith, J. Chem. Phys., 21 (1953) 1731.
17 M.J.S. Dewar, Bull. Soc. Chim. Fr., 18 (1951) C79.
18 J. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2939.
19 J.H. Nelson, K.S. Wheelock, L.C. Cusachs and H.B. Jonassen, J. Amer. Chem. Soc., 91 (1969) 9005.
20 R.W. Taft, Jr., in M.S. Newman (Ed.), Steric Effects in Organic Chemistry, J. Wiley, New York, 1956, p. 556.
21 P.L. Stanghellini, R. Rossetti, O. Gambino and G. Cetini, Inorg. Chim. Acta, in press.
22 K. Nakanishi, Infrared Absorption Spectroscopy, Nankodo Co. Lt., Tokyo, 1962.
23 G. Englert and A. Saupe, Mol. Cryst., 1 (1966) 503.
24 A.A. Bothner-By and C. Naar-Colin, J. Amer. Chem. Soc., 83 (1961) 231.
25 R.B. King, Inorg. Chim. Acta, 2 (1968) 454.
26 R.D. Kross, V.A. Fassel and M. Margoshes, J. Amer. Chem. Soc., 78 (1956) 1332.