The Electronic Polarizability Distribution of Several Substituted Ferrocenes and Di(η^6-benzene)chromium

Leonidas Phillips[*,a] **and Gary R. Dennis**[b]
[a] *Department of Physical Chemistry, University of Sydney, Sydney 2006, Australia*
[b] *Department of Chemistry, University of Western Sydney-Nepean, Kingswood 2747, Australia*

The polarizability tensor was investigated as a function of group additivity for a series of substituted ferrocenes and di(η^6-benzene)chromium. The findings yielded the sign of the polarizability anisotropy for several molecules. An analysis of the stretching force constants gave the metal atom charges for ferrocene, decamethylferrocene and di(η^6-benzene)chromium.

A strong additivity in the physical properties such as the stretching force constants,[1] dipole moments,[2] microwave relaxation times[3] and electrochemistry[4,5] has been found for the ferrocenyl system. This prompted an investigation of the electronic polarizabilities of ferrocene, [Fe(η-C_5H_5)$_2$], and selected derivatives to probe further the nature of the organometallic environment, and in particular, to yield a quantitative measure of the interaction between the iron atom and the complexed cyclopentadienyl rings. Molecular properties of di(η^6-benzene)chromium, [Cr(η-C_6H_6)$_2$], were also measured to allow a comparison with the charge distributions of these molecules and to gauge the effect that complexation of a metal has upon the free benzene ring properties.

Theory

(*i*) *Kerr effect and Molar Refraction.*—For the axially symmetric molecules investigated, each of which has a three-fold or higher-order rotation axis (subscripted z), the infinite dilution molar Kerr constant, $_\infty({}_mK_2)$, yields the polarizability anisotropy, $\Delta\alpha$, through the following theoretical expression [equation (1)],[6,7] where N_A, k_B, ε_o, μ and T are defined as

$$
\begin{aligned}
{}_\infty({}_mK_2) &= \frac{N_A}{81\varepsilon_o}\left\{\gamma^K + \frac{1}{k_BT}\left[\frac{2}{3}\mu\beta^K + \frac{1}{5}\Delta\alpha^o\Delta\alpha\right] + \frac{1}{5k_B{}^2T^2}\mu^2\Delta\alpha\right\} \\
&= \frac{N_A}{405\varepsilon_o}\left\{5\gamma^K + \frac{1}{k_BT}\left[\left(\frac{\Delta\alpha^o}{\Delta\alpha}\right)(\Delta\alpha)^2\right] + \frac{1}{k_B{}^2T^2}\mu^2\Delta\alpha\right\} \qquad (1)
\end{aligned}
$$

previously,[2] $\Delta\alpha$ ($=\alpha_{zz} - \alpha_{xx}$) and $\Delta\alpha^o$ ($=\alpha_{zz}{}^o - \alpha_{xx}{}^o$) are the anisotropies in the optical (high frequency) and static polarizabilities respectively, β^K and γ^K are the first and second hyperpolarizabilities of which β^K was assumed to be negligible.

The dipolar contribution to the Kerr effect dominates equation (1) for the anisotropic dipolar molecules[8] in this study *e.g.* 1,2,3,4,5-pentamethylferrocene [Fe(η-C_5H_5)(η-C_5Me_5)] and 1,2,3,4,5-pentachloroferrocene [Fe(η-C_5H_5)(η-C_5Cl_5)]. If this requirement is met, it is possible quantitatively to determine the sign of the polarizability anisotropy from the Kerr effect. For the non-dipolar molecules, decamethylferrocene [Fe(η-C_5Me_5)$_2$] and di(η^6-benzene)chromium [Cr(η-C_6H_6)$_2$], there exists an ambiguity in the sign of $\Delta\alpha$ since for these $\Delta\alpha$ appears only as a squared term in equation (1).

The mean polarizability, $\alpha = [(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3]$, was derived from the experimental molar refraction, ${}_mR_2$, which for axially symmetric molecules is given by equation (2).

$$
\begin{aligned}
{}_mR_2 &= N_A\alpha/3\varepsilon_o \\
&= N_A(2\alpha_{xx} + \alpha_{zz})/9\varepsilon_o \qquad (2)
\end{aligned}
$$

Measurements of the torque induced on crystals of ferrocene in a magnetic field yielded the sign of the molecular magnetic anisotropy[9] ($\Delta\chi$) which was then used to determine the sign of $\Delta\alpha$ from the molar Cotton–Mouton constant.[10] However, the crystal-phase magnetic moments have not been obtained for the metallocenes studied in this work. A primary objective in this work was to determine the orientation of the major axis of the polarizability tensors of di(η^6-benzene)chromium and substituted ferrocenes, and hence the signs of the polarizability anisotropies, $\Delta\alpha$.

(*ii*) *Force Constants and Bond Charges determined from Infrared Data.*—The metal atom charge of the isoelectronic molecules ferrocene and di(η^6-benzene)chromium can be derived from infrared data. We adopt the model used by Ray and Parr[11] of a three-body oscillator, XYX, where the term body refers to the metal atom or the aromatic ring. This involves the stretching force constant, k_1, and the interaction force constant, k_{12}, determined by equations (3) and (4),

$$k_1 = \frac{40\pi^2c^2\nu_3^2M_x/N_A}{1 + (2M_x/M_y)} \qquad (3)$$

$$k_{12} = 20\pi^2c^2M_x[\nu_1^2 - \{\nu_3^2/[1 + (2M_x/M_y)]\}]/N_A \qquad (4)$$

respectively,[12] where M_x and M_y refer to ring and metal mass in atomic mass units respectively while ν_1 and ν_3 are the symmetric and asymmetric metal–ring stretching frequencies in wavenumbers.

The bond charge, $-qe$, may be calculated from the force constants using[11] equation (5) where R_e is the equilibrium

$$k_1 + k_{12} = 37q^2e^2/18R_e{}^3 \qquad (5)$$

bond length. The potential used in this model places charges of $+\frac{2}{3}$ qe on each body, thereby allowing the calculation of the metal atom charge, q_M. Relevant values of k_1, k_{12}, R_e and q_M are given in Table 4.

Experimental

Substituted ferrocenes[1] and di(η^6-benzene)chromium[15] were synthesized as reported. Di(η^6-benzene)chromium, an ex-

Table 1 The solution-state dielectric permittivity, density and refractivity data[a] and dipole moments

Molecule	$\alpha\varepsilon_1$	$10^{-3}\ \beta d_1{}^{b}$/kg m^{-3}	γn_1	$10^5\ {}_mR_2$ /m^3 mol^{-1}	$10^{40}\ \alpha$ /C m^2 V^{-1}	$10^{30}\mu^{c}$/C m
$[Fe(\eta\text{-}C_5Me_5)_2]$	0.327 ± 0.009	0.2313 ± 0.0006	0.1057 ± 0.0018	9.88 ± 0.04	43.60 ± 0.18	0 ± 0.01
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$	0.570 ± 0.022	0.2558 ± 0.0030	0.1038 ± 0.0028	7.46 ± 0.06	32.90 ± 0.24	3.00 ± 0.07
$[Fe(\eta\text{-}C_5H_5)_2]^{d}$	0.347 ± 0.011	0.3363 ± 0.0030	0.12 ± 0.03	5.00 ± 0.43	22.0 ± 1.9	0 ± 0.01
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Cl)]$	1.54 ± 0.07	0.372 ± 0.006	0.110 ± 0.005	5.42 ± 0.08	23.9 ± 0.4	4.97 ± 0.17
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Cl)]^{e}$	1.43 ± 0.10	0.3628 ± 0.0015	0.078 ± 0.006	5.31 ± 0.07	23.4 ± 0.3	5.74 ± 0.07
$[Fe(\eta\text{-}C_5H_4Cl)_2]$	1.61 ± 0.05	0.396 ± 0.004	0.112 ± 0.006	6.05 ± 0.11	26.7 ± 0.5	7.0 ± 0.6
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$	1.01 ± 0.03	0.4395 ± 0.0014	0.078 ± 0.008	7.00 ± 0.20	30.9 ± 0.9	5.80 ± 0.07
$[Fe(\eta\text{-}C_5Cl_5)_2]^{e}$	0.02 ± 0.03	0.438 ± 0.008	0.066 ± 0.005	10.88 ± 0.20	48.0 ± 0.9	0 ± 0.01
$[Fe(\eta\text{-}C_4PH_2Me_2)_2]^{f}$	1.87 ± 0.03	0.3189 ± 0.0013	0.1448 ± 0.0028	8.13 ± 0.05	35.84 ± 0.24	7.8 ± 0.5
$[Fe(\eta\text{-}C_4PH_2Me_2)_2]^{e}$	2.83 ± 0.07	0.2945 ± 0.0010	0.110 ± 0.05	7.92 ± 0.08	34.9 ± 0.4	8.91 ± 0.20
$[Cr(\eta\text{-}C_6H_6)_2]^{g}$	0.55 ± 0.09	0.359 ± 0.019	0.17 ± 0.04	6.1 ± 0.6	26.8 ± 2.6	0 ± 0.01

[a] Solvent is cyclohexane unless otherwise indicated; ${}_mR_2$ values were evaluated at 589 nm. [b] Given by $\Sigma\Delta d_i/\Sigma w_i$ where Δd_i is the incremental solution density parameter for a weight fraction w_i. [c] For homoannular molecules whose geometry would require a zero dipole molecule, a value of 0 ± 0.01 C m was adopted. The dipolar members have values derived from an earlier dielectric-loss study.[2] [d] The current permittivity and refractivity data are in agreement with refs. 17 and 18. [e] Solvent is benzene. [f] Bis(3,4-dimethylphospholyl)iron. [g] The permittivity and refractivity data are in agreement with ref. 17.

Table 2 Infinite-dilution molar Kerr constant, ${}_\infty({}_mK_2)$ and the polarizability anisotropy of ferrocene, di(η^6-benzene)chromium and substituted ferrocenes in cyclohexane at 298 K and 632.8 nm

Molecule	$10^{15}(\Delta K_{12}/w_2)_{w_2=0}$	δ	$10^{27}\ {}_\infty({}_mK_2)_{w_2=0}{}^{a}$/m^5 V^{-2} mol^{-1}	$10^{40}\Delta\alpha^{b}$/C m^2 V^{-1}
$[Fe(\eta\text{-}C_5Me_5)_2]$	1.94 ± 0.05	3.50 ± 0.08	19.2 ± 0.8	6.69 ± 0.14
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$	7.97 ± 0.14	14.4 ± 0.3	55.7 ± 1.0	4.92 ± 0.34
$[Fe(\eta\text{-}C_5H_5)_2]^{c}$	3.44 ± 0.15	6.19 ± 0.47	17.9 ± 1.3	6.62 ± 0.29
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$	7.89 ± 0.39	14.2 ± 0.7	74.7 ± 3.7	2.16 ± 0.22
$[Cr(\eta\text{-}C_6H_6)_2]^{c}$	18.3 ± 3.8	32.9 ± 6.9	102 ± 21	15.7 ± 1.6

[a] $\gamma^K = (1.6 \pm 0.8) \times 10^{-60}$ C m^4 V^{-3}, which is twice the benzene value.[19] [b] $\Delta\alpha^0/\Delta\alpha = 1.05$. [c] $\Delta\alpha^0/\Delta\alpha = 1.00$.

Table 3 Carbon-13 NMR solution-state chemical shifts[a] of metallocenes studied

Molecule	Solvent	Nucleus	δ_C
$[Fe(\eta\text{-}C_5Me_5)_2]$	C_6D_{12}	C_5Me$_5$	78.73
		Me	9.84
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$	C_6D_{12}	C_5Me$_5$	80.29
		C_5H_5	71.53
		Me	11.66
$[Fe(\eta\text{-}C_5H_5)_2]$	C_6D_{12}	C_5H_5	68.28
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$	C_6D_{12}	C_5Cl_5	88.18
		C_5H_5	79.64
$[Fe(\eta\text{-}C_5Cl_5)_2]^{b}$	C_6D_6	C_5Cl_5	90.56
$[Cr(\eta\text{-}C_6H_6)_2]$	C_6D_{12}	C_6H_6	74.90
	C_6D_6	C_6H_6	74.93
C_6H_6	C_6D_{12}	C_6H_6	128.79
C_6Cl_6	C_6D_{12}	C_6Cl_6	133.15

[a] All chemical shifts referenced to SiMe$_4$. Most spectra were recorded on a JOEL FX-60Q instrument. [b] Bruker WM-400 instrument.

tremely water- and air-sensitive compound, was recrystallized from dry cyclohexane under nitrogen, and then sublimed immediately before measurements. Substituted ferrocenes were purified by vacuum sublimation and/or recrystallization. Solutions were prepared and manipulated under nitrogen. Cyclohexane was used as the solvent for the solution-phase measurements, and was purified and dried by distillation under nitrogen from phosphorus pentaoxide.

The infinite dilution molar Kerr constant, ${}_\infty({}_mK_2)$, is related to solution phase observables by equation (6), where F and J are

$$ {}_\infty({}_mK_2) = {}_sK_1\,(1 - \beta - F\gamma - J\alpha\varepsilon_1 + \delta)M_2 \qquad (6) $$

solvent constants,[16] β, γ, $\alpha\varepsilon_1$ and δ are the incremental density, refractive index, relative permittivity, and Kerr constant respectively, M_2 is the molecular weight of the solute and ${}_sK_1$ is the specific Kerr constant. Values for these constants and parameters are given in Tables 1 and 2.

The ^{13}C NMR chemical shifts, δ_C, of the metallocenes were measured in [$^2H_{12}$]cyclohexane or [$^2H_6$]benzene using either a JOEL FX-60Q or Bruker WM-400 spectrometer (Table 3). Solvent effects were minimized by using the non-dipolar, chemically unreactive and non-complexing solvent [$^2H_{12}$]cyclohexane, the protonated version of which was used as a solvent for the Kerr effect, microwave absorption[2,3] and polarization studies.

Inspection of the ^{13}C NMR chemical shifts of these compounds, given in Table 3, indicate a marked upfield displacement relative to their aromatic counterparts. It is interesting that the shielding of the ring carbons and the attached protons for ferrocene and di(η^6-benzene)chromium are similar.

Results and Discussion

(*i*) *Polarizability Analysis of Substituted Ferrocenes*.—For the dipolar molecules, $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$, the presence of a permanent dipole moment, μ, will result in the $\mu^2\Delta\alpha$ term dominating equation (1) and the sign of $\Delta\alpha$ may be obtained without any ambiguity. The polarizability anisotropies of these molecules are: $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ ($\Delta\alpha = 4.92 \times 10^{-40}$ C m^2 V^{-1}) and $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$ ($\Delta\alpha = 2.16 \times 10^{-40}$ C m^2 V^{-1}). However, only the magnitude of the polarizability anisotropy may be calculated from the Kerr effect for $[Fe(\eta\text{-}C_5Me_5)_2]$ ($\Delta\alpha = \pm 6.69 \times 10^{-40}$ C m^2 V^{-1}).

The axial and orthogonal components of the polarizability tensors for the methylated ferrocenes were evaluated using the polarizability anisotropies and equation (2). Two alternate sets of components were calculated for $[Fe(\eta\text{-}C_5Me_5)_2]$, one for $+\Delta\alpha$ and the second for $-\Delta\alpha$. Fig. 1 shows a plot of the polarizability components against the number of methyl substituents. It was expected that increasing methylation should have a linear effect on the magnitude of the polarizability components. This behaviour was found only if the polarizability components of decamethylferrocene were calculated using

Table 4 Stretching and interaction force constants with subsequent metal atom charges (q_M) for ferrocene and di(η^6-benzene)chromium

Molecule	10^{10} R_e[a]/m	k_1[b]/N m^{-1}	k_{12}/N m^{-1}	q_M[c]
[Fe(η-C_5H_5)$_2$]	1.661	263	48	1.16 ± 0.02
[Fe(η-C_5Me_5)$_2$]	1.662	356	−64	1.12 ± 0.02
[Cr(η-C_6H_6)$_2$]	1.613	276	39	1.11 ± 0.02

[a] Fe–C_5H_5 and Fe–C_5Me_5 distances are taken from ref. 13 while the Cr–C_6H_6 length is from ref. 14. [b] Values of k_1 are taken from ref. 1. [c] Errors in k_1 and k_{12} are 2 and 4 N m^{-1} respectively, with a variation of 0.01×10^{-10} m being adopted for the precision in R_e. These collective errors define the error in q_M, where q_M is in protonic charge units.

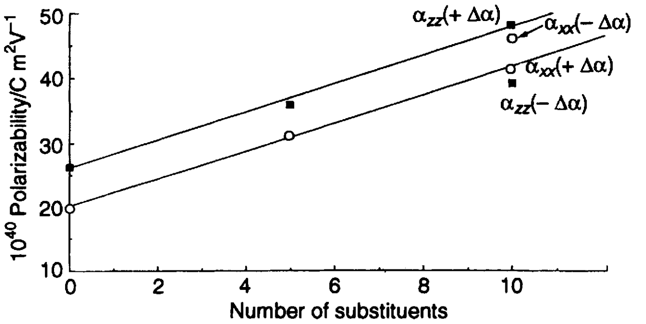

Fig. 1 Plot of components of the polarizability of methylated ferrocenes: ■ α_{zz} $y = 26.061 + 2.1647x$, $R^2 = 0.997$; ○ α_{xx} $y = 20.019 + 2.1577x$, $R^2 = 0.999$

a positive polarizability anisotropy. It was concluded that the polarizability anisotropy of [Fe(η-C_5Me_5)$_2$] is $\Delta\alpha = +6.69 \times 10^{-40}$ C m^2 V^{-1}.

(*ii*) *Polarizability Distribution and the Resultant Anisotropy in* [Cr(η-C_6H_6)$_2$].—The polarizability anisotropy of [Cr(η-C_6H_6)$_2$] was calculated from the Kerr constant to be $\Delta\alpha = \pm(15.7 \pm 1.6) \times 10^{-40}$ C m^2 V^{-1}. Two possible sets of values may be calculated for the polarizability components: set 1 (if $\Delta\alpha = -15.7$ then $\alpha_{zz} = 16.3$ and $\alpha_{xx} = 32.0$); and set 2 (if $\Delta\alpha = +15.7$ then $\alpha_{zz} = 37.3$ and $\alpha_{xx} = 21.6$). The polarizability components for benzene are $\alpha_{zz} = 8.8$ and $\alpha_{xx} = 13.0$.

It is expected that the axial component of the polarizability of the complex should increase compared to that of the isolated rings. Further, the orthogonal component should be relatively unaffected or slightly reduced due to redistribution of electron density into the metal–ring bond. Set 2 is consistent with these expectations, while the values for Set 1 are similar to the values expected for the isolated rings. From this we conclude that the polarizability anisotropy of [Cr(η-C_6H_6)$_2$] is $+(15.7 \pm 1.6) \times 10^{-40}$ C m^2 V^{-1}. It is noteworthy that the *average* polarizability of [Cr(η-C_6H_6)$_2$] is only about 16% greater than for two free benzene rings,[16] emphasizing it is the distribution of polarizability that is the cause of the large observed anisotropy.

The polarizability anisotropy of di(η^6-benzene)chromium is larger than ferrocene, and this has been observed in other complexes of chromium. It appears to be due to an exaltation of the axial polarizability, as evidenced by studies[20] of the polarizabilities of arenechromium tricarbonyl complexes and the appropriate free ligands. Aroney *et al.*[20] find that by subtracting the Cr(CO)$_3$ group polarizabilities from those of arenechromium tricarbonyl complexes, the residual arene–chromium is a highly polarizable system with the major polarizability axis in the Cr–arene bond direction. This was ascribed to the more polarizable π bonds between the chromium atom and the arene ligand. The effect would be accentuated even further in di(η^6-benzene)chromium, since the metal is now sandwiched between two arene ligands. Studies by the same group of workers on substituted chromium pentacarbonyls[21] [Cr(CO)$_5$L] where L = NMe_3 or PMe_3 verify that considerable polarizability augmentation occurs along the L–Cr axis when π bonding was present, *e.g.* where L = PMe_3 relative to the σ-bonded L–Cr complex [Cr(CO)$_5$(NMe_3)]

Any reduced aromaticity of the benzene ring upon complexation would diminish the in-plane polarizability of this ligand. Evidence for this comes from the longer C–C bond length[14] and the dramatic reduction in transmission of substituent effects across the complexed ring, possibly due to quenching of the delocalised π-electron system by donation into vacant metal orbitals upon complexation.[22,23] This latter idea was supported by UV-photoelectron spectra (PES) of di(arene)chromium complexes which indicate that interaction between the vacant e_{1g} metal MO and an occupied arene MO should lead to a degree of bonding.[24] An earlier PES study[25] and electron spectroscopy for chemical analysis (ESCA) investigations[13,26] indicated an increase of electron density on the complexed ring, consistent with a positive charge on the chromium atom. Multiphoton ionization spectra of di(η^6-benzene)chromium clearly show that the benzene ligand ejected has undergone a transformation away from the ground-state benzene.[27] The similarity in the metal–ring bond lengths, derived from the structures of [Fe(η-C_5H_5)$_2$][28,29] and [Cr(η-C_6H_6)$_2$],[14] indicate uniform bond characteristics.

(*iii*) *Metal Atom Charges.*—The charge on the iron atom in ferrocene was calculated to be +1.16 ± 0.02 protonic units (Table 4). This may be compared with estimates obtained from *ab initio* MO calculations[30,31] where $q_{Fe} = +1.2$ units. This value is also in accord with those from the *ab initio* calculations by Coutière *et al.*[32] and from the HFS Xα method by Baerends and Ros.[33] Applying the same analysis to decamethylferrocene gives a charge of $q_{Fe} = +1.12 \pm 0.02$ protonic units, effectively equivalent to the iron atom charge in ferrocene. This reduction in the metal was confirmed by the iterative extended Hückel theory calculations of Schmitz *et al.*[34] The charge on the Cr atom in di(η^6-benzene)chromium was calculated to be $q_{Cr} = +1.11 \pm 0.02$ protonic units, and this was confirmed by the X-ray absorption studies of Barinsky[35] who determined a chromium charge of $q_{Cr} = +1.10$ protonic units.

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References

1 L. Phillips, A. R. Lacey and M. K. Cooper, *J. Chem. Soc., Dalton Trans.*, 1988, 1383.

2 L. Phillips and S. W. Filipczuk, *J. Mol. Liq.*, 1991, **47**, 261.

3 S. W. Filipczuk and L. Phillips, *J. Mol. Liq.*, 1994, **59**, 13.

4 K. N. Brown, P. T. Gulyas, P. A. Lay, N. S. McAlpine, A. F. Masters and L. Phillips, *J. Chem. Soc., Dalton Trans.*, 1993, 835.

5 D. S. Fleming, K. N. Brown, P. T. Gulyas, P. A. Lay, A. F. Masters and L. Phillips, unpublished work.

6 M. R. Battaglia and G. L. D. Ritchie, *J. Chem. Soc., Faraday Trans. 2*, 1977, 209.

7 M. J. Aroney, R. M. Clarkson, T. W. Hambley and R. K. Pierens, *J. Organomet. Chem.*, 1992, **426**, 331.

8 K. E. Calderbank, R. L. Calvert, P. B. Lukins and G. L. D. Ritchie, *Aust. J. Chem.*, 1981, **34**, 1835.

9 (*a*) L. N. Mulay and M. E. Fox, *J. Chem. Phys.*, 1963, **38**, 760; (*b*) R. Mathis, M. Sweeney and M. E. Fox, *J. Chem. Phys.*, 1964, **41**, 3652.

10 G. L. D. Ritchie, M. K. Cooper, R. L. Calvert, G. R. Dennis, L. Phillips and J. Vrbancich, *J. Am. Chem. Soc.*, 1983, **105**, 5215.

11 N. K. Ray and R. G. Parr, *J. Chem. Phys.*, 1973, **59**, 3934.

12 G. Herzberg, *Molecular Spectra and Molecular Structure II. IR and Raman Spectra of Polyatomic Molecules*, Van Nostrand-Reinhold, New York, 1945, pp. 172–400.

13 H. Binder and C. Elschenbroich, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 659.

14 A. Haaland, *Acta Chem. Scand.*, 1965, **19**, 41.

15 E. O. Fischer, *Inorg. Synth.*, 1960, **6**, 132.

16 G. L. D. Ritchie and J. Vrbancich, *Aust. J. Chem.*, 1982, **35**, 869.

17 E. Weiss, *Z. Anorg. Allg. Chem.*, 1956, **286–287**, 236.

18 W. Strohmeier and D. Hobe, *Z. Electrochem.*, 1960, **64**, 945.

19 M. P. Bogaard, A. D. Buckingham and G. L. D. Ritchie, *Mol. Phys.*, 1970, **18**, 575.

20 M. J. Aroney, M. K. Cooper, R. K. Pierens, S. J. Pratten and S. W. Filipczuk, *J. Organomet. Chem.*, 1985, **295**, 333.

21 M. S. Davies, R. K. Pierens and M. J. Aroney, *J. Organomet. Chem.*, 1993, **458**, 141.

22 V. Graves and J. J. Lagowski, *Inorg. Chem.*, 1976, **15**, 577.

23 N. Hao and M. J. McGlinchey, *J. Organomet. Chem.*, 1978, **161**, 381.

24 D. E. Cabelli, A. H. Cowley and J. J. Lagowski, *Inorg. Chim. Acta*, 1982, **57**, 195.

25 S. Evans, J. C. Green and S. E. Jackson, *J. Chem. Soc., Faraday Trans. 2*, 1972, 249.

26 S. Pignataro, A. Foffani and G. Distefano, *Chem. Phys. Lett.*, 1973, **20**, 350.

27 G. J. Fisanick, A, Gedanken, T. S. Eichelberger IV, N. A. Kuebler and M. B. Robin, *J. Chem. Phys.*, 1981, **75**, 5215.

28 A. Haaland and J. E. Nilsson, *Acta Chem. Scand.*, 1968, **22**, 2653; R. K. Bohn and A. Haaland, *J. Organomet. Chem.*, 1966, **5**, 470.

29 A. Almenningen, A. Haaland, S. Samdal, J. Brunvoll, J. L. Robbins and J. C. Smart, *J. Organomet. Chem.*, 1979, **173**, 293.

30 P. S. Bagus, U. I. Wahlgren and J. Almlöf, *J. Chem. Phys.*, 1976, **64**, 2324.

31 H. P. Lüthi, J. Ammeter, J. Almlöf and K. Faegri, jun., *J. Chem. Phys.*, 1982, **77**, 2002.

32 M.-M. Coutière, J. Demuynck and A. Veillard, *Theor. Chim Acta*, 1972, **27**, 281.

33 E. J. Baerends and P. Ros, *Chem. Phys. Lett.*, 1973, **23**, 391.

34 D. Schmitz, J. Fleischhauer, U. Meier, W. Schleker and G. Schmitt, *J. Organomet. Chem.*, 1981, **205**, 381.

35 R. P. Barinsky, *Zh. Strukt. Khim.*, 1960, **1**, 200.

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