Journal of Organometallic Chemistry, 51 (1973) 289–295

ROTATIONAL ISOMERISM IN MOLYBDENUM AND TUNGSTEN TETRACARBONYL COMPLEXES OF OLEFINIC TERTIARY PHOSPHINES AND ARSINES

M. A. BENNETT and I. B. TOMKINS

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600 (Australia)

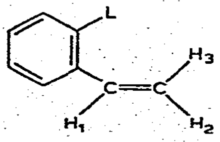
(Received September 11th, 1972)

SUMMARY

The ligands *o*-styryldiphenylarsine [(*o*-vinylphenyl)diphenylarsine], SPA, *o*-CH_2=$CHC_6H_4AsPh_2$, and *o*-styryldimethylarsine [(*o*-vinylphenyl)dimethylarsine], SMA, *o*-CH_2=$CHC_6H_4AsMe_2$ form Group VI tetracarbonyl complexes of general formula $M(CO)_4L$ (L=SPA, M=Cr, Mo or W; L=SMA, M=Mo or W) in which both the arsenic atoms and the olefinic double bonds are coordinated. The complexes are similar to, but less stable than, the corresponding complexes of *o*-styryldiphenylphosphine [(*o*-vinylphenyl)diphenylphosphine], SPP, *o*-CH_2=CHC_6H_4-PPh_2. The IR spectra in the C≡O stretching region of solutions of the molybdenum and tungsten carbonyl complexes of SPP, SPA and SMA show that two isomers are present in each case. It is suggested that these isomers differ in the orientation of their coordinated double bonds, and that interconversion between the two orientations, which is rapid on the NMR time scale, occurs by rotation about the metal to Group V element and metal–olefin bond axes.

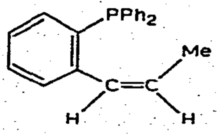
INTRODUCTION

Earlier papers[1,2] have reported the preparation of Group VI transition metal tetracarbonyl complexes formed by the olefinic tertiary phosphines *o*-styryldiphenylphosphine [(*o*-vinylphenyl)diphenylphosphine] (SPP), (Ia), (*o*-*cis*-propenylphenyl)diphenylphosphine (*cis*-PPP), (II), and its *trans*-isomer (*trans*-PPP), (III). The complexes $M(CO)_4$(*cis*-PPP) (M=Cr, Mo, or W) are formed by isomerisation of

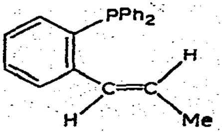


(I)

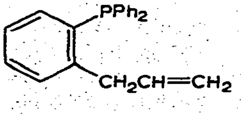
(a) L = PPh_2(SPP)
(b) L = $AsPh_2$(SPA)
(c) L = $AsMe_2$(SMA)



(II) (*cis*-PPP)



(III) (*trans*-PPP)



(IV) (APP)

(o-allylphenyl)diphenylphosphine(APP), (IV), in the presence of the Group VI metal hexacarbonyls[2], and an X-ray single crystal structural determination of $M(CO)_4$(*cis*-PPP)[3] has confirmed that both the Group V atom and the olefinic double bond are coordinated. We now report analogous complexes of o-styryldiphenylarsine(SPA), (Ib), and o-styryldimethylarsine(SMA), (Ic), and we present evidence which indicates the presence of conformational isomers in the tetracarbonylmolybdenum and tetracarbonyltungsten complexes of SPP, SPA and SMA.

RESULTS AND DISCUSSION

The ligand SPA reacts with $M(CO)_4(NBD)$ {M=Cr, Mo, or W; NBD= bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)} in refluxing benzene to give the yellow, crystalline complexes of general formula $M(CO)_4$(SPA), which are similar in appearance and properties to the analogous SPP complexes[1], but are somewhat less stable towards aerial oxidation, especially in solution. A similar procedure affords $Mo(CO)_4$(SMA), which could only be obtained in a pure state in 10–20% yield. The tungsten complex $W(CO)_4$(SMA) could not be obtained analytically pure, but it was identified by NMR, IR and mass spectrometry. Attempts to isolate any product from the reaction of SMA with $Cr(CO)_4(NBD)$ have been unsuccessful.

The proton NMR spectra of the complexes of SPA and SMA are very similar to the ^{31}P-decoupled spectra of the SPP complexes (Table 1). A characteristic feature is the large upfield shift of the vinyl proton resonances on coordination, an effect which is especially noticeable for the *trans*-β-proton H_3; this appears at higher field than the *cis*-β-proton H_2 in the complexes, but is at lower field than H_2 in the free ligands. The magnitudes of the *cis*- and *trans*-vicinal coupling constants ($|J_{12}|$ and

TABLE 1

PROTON NMR DATA FOR OLEFINIC LIGANDS AND THEIR GROUP VI CARBONYL COMPLEXES[a,b]

Compound	*Solvent*	*δ(Aromatic protons)*	*δ(H₁)*	*δ(H₂)*	*δ(H₃)*	$\|J_{12}\|$	$\|J_{13}\|$	$\|J_{23}\|$
SPP	C_6D_6	6.8–7.8 m	[c]	4.99 dd	5.45 t	11.0	17.5	1.3[e]
SPP[d]	$CDCl_3$	7.0–7.6 m	~6.8 m	5.14 dd	5.60 t			
SPA	C_6D_6	6.8–7.5 m	[c]	5.01 dd	5.48 dd	11.0	17.5	1.3
	$CDCl_3$	6.8–7.6 m	7.10 q	5.21 dd	5.60 dd			
SMA	$CDCl_3$	7.2–7.6 m	[c]	5.26 dd	5.60 dd[f]	11.0	17.5	1.5
$Cr(CO)_4$(SPP)	C_6D_6	7.0–8.0 m	5.06 (7 lines)	3.25 dd	2.86 dd	9.0	13.0	0[g]
$Cr(CO)_4$(SPA)	C_6D_6	6.52–7.50 m	5.16 dd	3.32 d	2.79 d	9.8	13.5	~0
$Mo(CO)_4$(SPA)	C_6D_6	6.56–7.50 m	5.49 dd	3.54 d	3.15 d	9.8	14.0	~0
$W(CO)_4$(SPA)	C_6D_6	6.55–7.50 m	5.15 dd	3.39 d	2.90 d	9.8	13.5	~0
$Mo(CO)_4$(SMA)	C_6D_6	6.60–7.20 m	5.45 dd	3.56 d	2.37 d[h]	9.8	13.5	<0.5
$W(CO)_4$(SMA)	C_6D_6	6.60–7.20 m	5.13 dd	3.45 d	2.63 d[i]	9.6	13.5	<0.5

[a] Chemical shifts (δ) are in ppm downfield of internal TMS. Protons are numbered as in (I). Coupling constants (*J*) are probably accurate to within ±0.2 Hz. [b] Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet. [c] Beneath aromatic resonances. [d] Values from ref. 1. [e] $|J(P-H_2)| = 1.1$ Hz. [f] $AsMe_2$ resonance at δ 1.05. [g] Incorrectly given in ref. 1 as 5.0 Hz (see text); $|J(P-H_2)| = |J(P-H_3)| = 5.0$ Hz; $|J(P-H_1)| \sim 2.0$ Hz. [h] $AsMe_2$ resonances at δ 0.87, 0.95. [i] $AsMe_2$ resonances at δ 0.95, 1.02.

$|J_{13}|$) also decrease on coordination but the geminal coupling constant ($|J_{23}|$) remains less than 0.5 Hz, indicating that the HCH bond angle is still close to 120° in the complexes. It should be noted that the splittings which were previously ascribed[1] to geminal coupling ($|J_{23}|$) in the complexes $M(CO)_4(SPP)$ are in fact due to ^{31}P–^{1}H coupling, and the discussion in that paper concerning possible changes in the HCH bond angle on coordination is invalid. It happens that $|J(P\text{–}H_1)|$ and $|J(P\text{–}H_2)|$ are equal for each of the $M(CO)_4(SPP)$ complexes (M = Cr, 5.0 Hz; M = Mo, 2.5 Hz; M = W, 3.0 Hz).

The IR spectra of SPP, SPA and SMA show a weak band at 1625–1630 cm^{-1} assignable to the C=C stretching frequency, and bands in the region of 990 and 920 cm^{-1} due to C–H out-of-plane deformations. In the complexes $M(CO)_4(SMA)$ (M = Mo or W), weak bands at ca. 1490 cm^{-1} and 1240 cm^{-1} (Table 2) can be assigned to coupled modes involving C=C stretching and CH_2 deformation, following the most recent assignments for mono-olefin complexes of platinum(II)[4–6]. In the complexes $M(CO)_4(SPA)$ (M = Cr, Mo or W), the expected band in the 1490 cm^{-1} region could not be located, presumably owing to its low intensity. We have also been unable to confirm previous observations[1] of weak bands in the 1490–1500 cm^{-1} region of the $M(CO)_4(SPP)$ complexes. These were originally assigned to the C=C stretching mode modified by coordination, but clearly definitive assignment must await Raman spectroscopic studies.

The $\nu(CO)$ values of all the Group VI tetracarbonyl complexes in cyclohexane or hexane solution are given in Table 2, and the spectra of the SPP complexes in the 2000 cm^{-1} region are shown in Fig. 1. Previously[1] only mull spectra for the

TABLE 2

INFRARED DATA (cm^{-1}) FOR OLEFINIC LIGANDS AND THEIR GROUP VI CARBONYL COMPLEXES[a]

Compound	*ν(CO)(Solution)*[b]	*ν(CO)(Nujol)*	*ν(C=C) + δ(CH$_2$) (KBr disc)*
SPA			1625 w
SMA			1629 m[c]
$Cr(CO)_4(SPP)$	2039(9), 1953(9.5), 1933(10), 1912(9.5)[d]	2015, 1930, 1905, 1885[f,g]	1245 w[g]
$Cr(CO)_4(SPA)$	2030(8), 1949(8), 1932(10), 1907(9.5)[e]	2029, 1943, 1914, 1874[f]	1245 w
$Mo(CO)_4(SPP)$	2044(5.5), 1958(7.5), 1945(10), 1929(7.5), 1916(8.5)[d]	2035, 1950, 1910, 1885[f,g]	1246 w[g]
$Mo(CO)_4(SPA)$	2042(8), 1954(8.5), 1944(10), 1927(7.5), 1910(9)[e]	2044, 1951, 1925, 1876[f]	1245 w
$Mo(CO)_4(SMA)$	2039(8), 1948(sh)(9.5), 1942(10), 1924(9), 1909(9)[d]	2038, 1939, 1922, 1891[f]	1495 w(?), 1241 m
$W(CO)_4(SPP)$	2034(4.5), 1950(4), 1937(10), 1928(sh)(3), 1915(4), 1907(5)[d]	2030, 1945, 1910, 1880[f,g]	1236 w[g]
$W(CO)_4(SPA)$	2043(7), 1952(7), 1941(10), 1930(3.5), 1919(5.5), 1907(8.5)[e]	2042, 1946, 1920, 1870[f]	1237 m
$W(CO)_4(SMA)$	2043(7.5), 1948(7), 1940(10), 1925(4), 1916(7), 1905(8.5)[e]	2043, 1939, 1915, 1905[f]	1480 w(?), 1232 m

[a] Abbreviations: (sh), shoulder; m, medium; w, weak. [b] Figures in parentheses represent intensities (±0.5) relative to the most intense peak at ~1940 cm^{-1} (10 units), measured from an arbitrary base line. [c] Measured on neat liquid [d] Measured in n-hexane. [e] Measured in cyclohexane. [f] All bands strong. [g] Values from ref. 1.

SPP complexes had been recorded. Both $Cr(CO)_4(SPP)$ and $Cr(CO)_4(SPA)$ show the four bands expected[7,8] for a *cis*-disubstituted octahedral metal carbonyl, but the complexes $Mo(CO)_4(SPP)$, $Mo(CO)_4(SPA)$ and $Mo(CO)_4(SMA)$ show five well-resolved maxima, and the corresponding tungsten complexes show six bands. The relative intensities of these bands vary reversibly with temperature. Thus, on cooling a solution of $W(CO)_4(SPP)$ in n-hexane to −80°, the bands at 1950 cm^{-1} and 1928 cm^{-1} increase in intensity relative to that at 1937 cm^{-1}, and the band at 1907 cm^{-1} increases relative to that at 1915 cm^{-1}. For $Mo(CO)_4(SPP)$, the band at 1927 cm^{-1} decreases in relative intensity on cooling to −80°. The largest shift in the band maxima observed on cooling is 2–3 cm^{-1}, and the smallest separation of band maxima for these two complexes is 8–9 cm^{-1}. The IR spectrum of $Cr(CO)_4(SPP)$ does not change when the temperature is lowered.

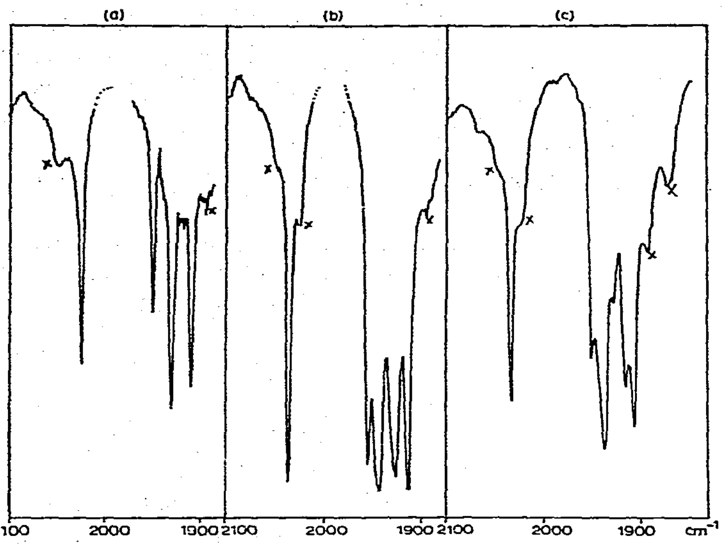


Fig. 1. Bands due to $\nu(CO)$ at room temperature in n-hexane of (a) $Cr(CO)_4(SPP)$; (b) $Mo(CO)_4(SPP)$; (c) $W(CO)_4(SPP)$. X = Band due to solvent.

The observations suggest that solutions of the $Mo(CO)_4$ and $W(CO)_4$ complexes of SPP, SPA and SMA contain two isomers in equilibrium, but owing to the proximity of the $\nu(CO)$ bands, it is not possible to estimate the amount of each isomer present. We suggest that the isomers have different orientations of the coordinated olefin. Figure 2 shows that the double bond in the Group VI tetracarbonyl complexes could lie either in, or perpendicular to the plane defined by the Group V atom and the equatorial carbonyl groups. This possibility has also been recognised by Truter and co-workers[3], but their X-ray study of $(cis\text{-}PPP)Mo(CO)_4$ shows that in this compound the double bond lies almost in the equatorial coordination plane in the solid state; there is no evidence from the infrared spectra for the existence of a second isomer in solution either at room temperature or at −80° [$\nu(CO)$ (n-hexane) 2036, 1939 and 1920 cm^{-1}]. Truter *et al.*[3] suggest that the axial orientation of the double bond in $Mo(CO)_4(cis\text{-}PPP)$ may be destabilised by steric hindrance between the methyl group and one of the phenyl rings. In the cases of $Cr(CO)_4(SPP)$ and $Cr(CO)_4(SPA)$,

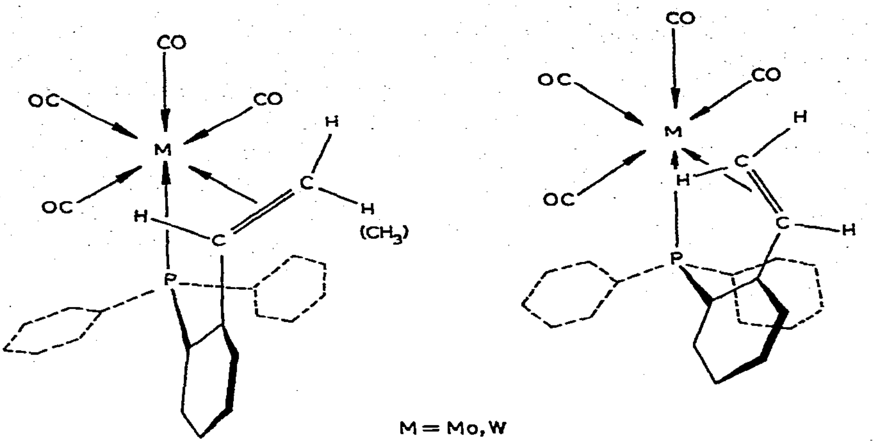


Fig. 2: Rotational isomers of $M(CO)_4(SPP)$. The equatorial orientation is adopted by $Mo(CO)_4$(*cis*-PPP) in the solid state.

it is impossible to say whether only one isomer is present in solution, or whether the bands due to $\nu(CO)$ of two isomers are unresolvable.

The proton NMR spectrum of $W(CO)_4(SP)$ in CD_2Cl_2 remains essentially unchanged from room temperature to $-90°$, below which temperature the complex crystallises. This observation suggests either that the two isomers have identical chemical shifts, which seems unlikely, or that they are interconverting rapidly such that, even at $-90°$, only a time-averaged spectrum results. This could occur by dissociation of the olefin from the metal, giving a five-coordinate intermediate, followed by return of the olefin in the alternative orientation. This possibility can be ruled out on the grounds that the interconversion is much faster than the S_N1-type substitution processes generally observed for Group VI metal hexacarbonyls and their derivatives[9], and also that the P–H coupling of 3.5 Hz to the β-protons in $W(CO)_4(SPP)$ is retained down to $-90°$, whereas in the free ligand this coupling is close to zero. A more likely possibility, as judged by examination of Dreiding models, involves rotation of the double bond about the metal–olefin axis concomitant with rotation about the metal to Group V element, Group V element to phenyl carbon and phenyl carbon to α-vinyl carbon bonds. Since these are essentially single bonds, the barrier to rotation about the metal–olefin axis could be lower than those in ethylene complexes of rhodium(I)[10,11] and platinum(II)[12,13]. Related behaviour has been observed in the complex *cis*-$Mo(CO)_4(PPh_2H)_2$, for which two crystalline forms with different IR spectra have been isolated[14]. It was suggested that these are *sym* (H's adjacent) and *asym* (H's non-adjacent) rotamers derived by restricted rotation about the Mo–P bond, although in solution only one rotamer, probably the *sym*, appears to be present. Similar restricted rotation in the complexes of sterically hindered ligands such as di-tert-butylethylphosphine[15], t-Bu_2EtP, gives rise to rotamers which interconvert fairly slowly at room temperature on the NMR time scale.

EXPERIMENTAL

IR spectra were recorded on Perkin–Elmer 457 and 225 spectrophotometers calibrated with polystyrene. Solid state spectra were taken either as KBr discs or as Nujol mulls on KBr windows, solution spectra were measured in 1 mm path-length cells using KBr windows. An R.I.I.C. VLT-2 1 mm path length cell employing acetone/dry ice as coolant and a calibrated direct-reading thermocouple was used for variable temperature solution spectra. Proton NMR spectra were recorded on Varian HA-100 and Jeol C60-HL instruments using TMS as internal reference (Mr. C. Arandjelovic) and mass spectra were measured on an AEI MS-9 instrument at 70 eV (Mr. K. Goggin). Analyses (Table 3) are by the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research at the Australian National University (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates).

TABLE 3

ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compound	*Colour*	*M.p.* (°C)[a]	*Analysis found (calcd.)(%)*	
			C	*H*
o-CH_2=$CHC_6H_4AsPh_2$(SPA)	White	68–70	72.2 (72.3)	5.4 (5.2)
$Cr(CO)_4$(SPA)	Deep yellow	120–125 (dec.)	58.0 (58.1)	3.3 (3.5)
$Mo(CO)_4$(SPA)	Yellow	135–140 (dec.)	53.6 (53.3)	3.5 (3.2)
$W(CO)_4$(SPA)	Pale yellow	145–150 (dec.)	46.0 (45.8)	3.3 (2.7)
$Mo(CO)_4$(SMA)	Pale yellow	75–78 (dec.)	39.4 (40.4)	3.7 (3.2)

[a] Determined in sealed capillaries under nitrogen; uncorrected.

Solvents and starting materials

n-Hexane and n-pentane were dried over molecular sieves (B.D.H. type 4A) and degassed before use. A.R. grade benzene, tetrahydrofuran and diethyl ether were dried over sodium wire. The ligands *o*-styryldiphenylphosphine[16] and *o*-styryldimethylarsine[17], and the Group VI metal tetracarbonyls of norbornadiene[18,19] were prepared by literature methods. *o*-Styryldiphenylarsine was prepared similarly to *o*-styryldiphenylphosphine. From *o*-bromostyrene (17.3 g, 0.095 mol), magnesium (2.3 g, 0.095 mol) and chlorodiphenylarsine (25 g, 0.095 mol) was obtained 19 g (61 %) of *o*-styryldiphenylarsine after one recrystallisation from n-pentane.

Preparation of ligand metal tetracarbonyls

The procedure was essentially similar to that used for $M(CO)_4$(SPP) (M = Cr, Mo or W)[1]. The appropriate $M(CO)_4$(NBD) complex (0.5 g) was heated under reflux in benzene (40 ml) with one mole equivalent of the ligand in a nitrogen atmosphere for 3.5–4 h. The solvent was removed at 15 mm, the residue was washed with n-pentane (2 × 5 ml) at −78°, and then extracted with boiling n-hexane (25–30 ml) under nitrogen. The solution was filtered and allowed to stand overnight in the refrigerator.

The colorless or yellow crystals were washed with ice-cold isopentane (2 × 3 ml.) and dried *in vacuo*. Yields of the $M(CO)_4(SPA)$ complexes were 50–70%, those of the SMA complexes 10–20%. In the preparation of $W(CO)_4(SMA)$ from $W(CO)_4(NBD)$, some $W(CO)_6$ was also formed, and was removed by sublimation at 25°/10^{-2} mmHg. The product tenaciously retains the hydrocarbon solvents used for recrystallisation, but its identity was confirmed by its proton NMR spectrum (Table 1) and by its mass spectrum, which shows a parent ion peak and peaks due to the successive loss of four CO groups. The $M(CO)_4(SPP)$ and $M(CO)_4(SPA)$ complexes show similar mass spectra.

ACKNOWLEDGEMENT

We thank Mrs. K. Hoskins for the synthesis of *o*-styryldiphenylarsine.

REFERENCES

1 M. A. Bennett, R. S. Nyholm and J. D. Saxby, *J. Organometal. Chem.*, 10 (1967) 301.
2 L. V. Interrante, M. A. Bennett and R. S. Nyholm, *Inorg. Chem.*, 5 (1966) 2212.
3 H. Luth, M. R. Truter and A. Robson, *J. Chem. Soc. A*, (1969) 28.
4 J. Hiraishi, *Spectrochim. Acta, Part A*, 25 (1969) 749.
5 J. Hiraishi, D. Finseth and F. A. Miller, *Spectrochim. Acta, Part A*, 25 (969) 1657.
6 D. B. Powell, J. G. V. Scott and N. Sheppard, *Spectrochim. Acta, Part A* 28 (1972) 327.
7 L. E. Orgel, *Inorg. Chem.*, 1 (1962) 25.
8 F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84 (1962) 4432.
9 R. J. Angelici, *Organometal. Chem. Rev.*, 3 (1968) 173, and references cited therein.
10 R. Cramer, *J. Amer. Chem. Soc.*, 86 (1964) 217.
11 R. Cramer, J. B. Kline and J. D. Roberts, *J. Amer. Chem. Soc.*, 91 (1969) 2519.
12 C. E. Holloway, G. Hulley, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, (1969) 54.
13 C. E. Holloway, G. Hulley, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, (1970) 1653.
14 J. G. Smith and D. T. Thompson, *J. Chem. Soc. A*, (1967) 1694.
15 B. E. Mann, C. Masters, B. L. Shaw and R. E. Stainbank, *J. Chem. Soc. D*, (1971) 1103.
16 M. A. Bennett, W. R. Kneen and R. S. Nyholm, *J. Organometal. Chem.*, 26 (1971) 293.
17 M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long and R. S. Nyholm, *J. Chem. Soc. A*, (1967) 501.
18 M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1961) 2037.
19 R. B. King and A. Fronzaglia, *Inorg. Chem.*, 5 (1966) 1837.