Journal of Organometallic Chemistry, 266 (1984) 139–146
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

"NUT-IN-THE-NUTSHELL" TYPE OF METAL CLUSTER COORDINATION BY THE LIGANDS. X-RAY INVESTIGATION OF TWO CARBONYL CLUSTERS $[RhFe_5C(CO)_{16}]^-$ AND $[Rh_5Fe(CO)_{16}]^-$ WITH A SPECIFIC DISORDER OF THE METAL POLYHEDRON

Yu.L. SLOVOKHOTOV, Yu.T. STRUCHKOV*, V.E. LOPATIN and S.P. GUBIN

Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vavilova St. 28, Moskow B-312, (U.S.S.R.)

(Received November 10th, 1983)

Summary

An X-ray investigation of the two tetraethylammonium salts, $Et_4N^+[RhFe_5C(CO)_{16}]^-$ (I) and Et_4N^+ $[Rh_5Fe(CO)_{16}]^-$ (II) containing octahedral cluster anions (−120°C, λ(Mo), $R = 0.035$ (I) and 0.033 (II)) has been carried out. In both anions identical CO-ligand configurations corresponding to the minimum ligand repulsion are realized. The orientation of the disordered M_5M' cluster nucleus relative to the CO-shell differs in I (12 terminal and 4 semi-bridging CO) and II (12 terminal and 4 μ_3-CO).

Introduction

At present a large number of octahedral transition metal carbonyl clusters are known [1–3]. Such clusters strictly follow Wade's "$2n + 2$" rule, i.e., have 7 skeleton electron pairs per 6 metal atoms which gives a total of 86 valence electrons. At the same time, both the composition of the molecule and the type of ligand coordination of the cluster may vary within rather broad limits in these compounds due to formation of "mixed" complexes with different metal atoms in the polyhedron, inclusion of light atoms (H or C) into the octahedron, as well as due to the high coordinating abilities of the CO ligands and their substitution by other ligands. Transition metals such as Fe and Rh are the most typical cluster-forming metals and readily form octahedral complexes of the above type. In the course of a systematic X-ray investigation of polyhedral systems we have determined the structures of two carbonyl anion clusters $[RhFe_5C(CO)_{16}]^-$ (I) and $[Rh_5Fe(CO)_{16}]^-$ (II): close analogs that are, in a sense, mutually complementary.

Experimental

The cluster anions I and II were obtained by thermolysis in diglyme of sodium amalgam-reduced $Fe(CO)_5$ and $RhCl_3$. The structure of the final product depends on the moment of addition of $RhCl_3$ at the different thermolysis stages.

0022-328X/84/$03.00 © 1984 Elsevier Sequoia S.A.

TABLE 1

BASIC X-RAY DATA FOR I AND II

	I	II
Composition	$Et_4N[RhFe_5C(CO)_{16}]$	$Et_4N[Rh_5Fe(CO)_{16}]$
Space group	$P4/n$	$P4/n$
a (Å)	12.875(5)	13.439(2)
c (Å)	9.755(3)	9.465(2)
Z	2	2
d_{calc} (g/cm^3)	2.00	2.23
T (°C)	−120	−120
Radiation	Mo-K_α	Mo-K_α
Scan	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$, deg	50	54
Total reflections	1346	1940
Number of observed reflections ($I > 2\sigma$)	1085	1783
Number of reflections in the final refinement	928	1598
R_1	0.035	0.033
R_2	0.040	0.062
G.O.F.	1.92	4.02

Heating of the reduced $Fe(CO)_5$ above 100°C yields the $[Fe_5C(CO)_{14}]^{2-}$ dianion [4] which is converted into I on addition of $RhCl_3$. The cluster II is obtained by heating the mixture of the reactants to 105–115°C.

The X-ray diffraction data for I and II were obtained on a 4-circle automatic Syntex $P2_1$ diffractometer at −120°C (Table 1). The structures of I and II were solved by direct methods using the MULTAN program and were refined by the least squares method in the block-diagonal (I) and full-matrix (II) approximations with anisotropic thermal parameters, but without a correction for the absorption. The cluster anions in the crystals of I and II occupy the special 2(a) positions of the $\bar{4}$-symmetry of the $P4/n$ space group with similar cell parameters, yet are not isostructural and are also different as regards the type of the metal atom disorder in the M_5M' octahedron. The positions of the metal clusters in both I and II correspond to a pseudo-base-centered lattice, which is responsible for the considerable attenuation of the odd-($h+k$) reflections of the general type. The Et_4N^+ cations are in both structures in the special 2(c) positions of the $\bar{4}$-symmetry, the alpha-carbons of the TEt groups are disordered at two positions, C(5) and C(5′), and given with half weights, and the beta-carbons C(6) have the same position in both cation orientations and are given with unit weights. The H atoms were not localized due to considerable disorder. The first step in the solution of the structures of I and II was carried out in the $P\bar{4}$ space group, where two independent cluster anions and the ordered Et_4N^+ counter ion lying on the 2 axis were detected. It should also be noted that certain reflections of the $h0l$ ($0kl$) type extinct in the $P\bar{4}/n$ space group have, in fact, intensities slightly exceeding three background level values. Thus it appears that the true space group of I and II is $P\bar{4}$, but the two cluster anions lying on the $\bar{4}$ axes in this group are, within error limits, coupled by an inversion center and similarly disordered (see below). In order to identify the structural parameters of the anions of I and II with better precision, the final refinement of the structures of I and II was carried out in the $P\bar{4}/n$ space group.

In the anions of I the Rh and Fe atoms occupy with equal probability both "axial" vertices on the $\bar{4}$ axis and were identified independently with half weights. In the anion II the Fe atom is statistically disordered at all the six octahedron vertices, therefore, we used for the metal atom a "mixed" scattering factor: $f_M = 1/6\ (5f_{Rh} + f_{Fe})$ (the f_{Rh} and f_{Fe} values were taken from ref. 5).

It should be noted that refinement of the models of the structure of II corresponding to the compositions: $Et_4N^+\ [FeRh_5(CO)_{16}]^-$ ("disordered model") and $Et_4N^+[Rh_6(CO)_{16}]^-$ ("ordered model") with the same number of independent parameters (117) for 1783 independent reflections with $I > 2\sigma$ gave R factor values of 0.037 and 0.042, respectively, on the basis of which we unequivocally opted for the "disordered" model and objectively demonstrated the composition of the cluster anion, also consistent with the "$2n + 2$" rule. The final values were R(I) = 0.035 and R(II) = 0.033 for 928 and 1598 reflections with $I > 4\sigma$, respectively. Coordinates of atoms and anisotropic temperature parameters are given in Table 2 for I and Table 3 for II. The computations were done on an Eclipse S/200 computer by the EXTL programs modified by A.I. Yanovsky and R.G. Gerr at the X-ray Diffraction Analysis Laboratory of the Institute of Organo-element Compounds.

Discussion

Despite the above-mentioned disorder of the structures of I and II, the accuracy of analysis permitted determination of the geometric parameters of the cluster anions with satisfactory precision. The most important bond lengths and valence angles of the anions are given in Table 4. The structure of I has been investigated for the first time; the closest analog of II with the same anion $[Rh_5Fe(CO)_{16}]^-$ and the $(Rh_3P)_2N^+$ cation (IIa) was recently studied by Italian investigators [6]. The Rh_5Fe clusters in II and IIa exhibit a similar disorder of the Fe atom at the octahedron vertices. The anions I and II obey Wade's rule which, therefore, "controls" their formation reactions: in order to attain the stable $2n + 2$-electron configuration, the $RhFe_5$ octahedron in I, which has 4 valence electrons less than the Rh_5Fe octahedron in II, while the charge and the number of CO ligands are the same, incorporates into the metal polyhedron the interstitial carbide C atom, the donor of the missing 4 e^-, whereas in II the octahedral cavity is unoccupied.

The structure of $[RhFe_5C(CO)_{16}]^-$

The anion I is shown in Fig. 1. The distances $Fe_{ax.}-Fe_{equat.} = 2.723(2)$ Å, $Fe_{equat.}-Fe_{equat} = 2.666(1)$ Å; the mean, 2.685 Å, is somewhat larger than the mean Fe–Fe distance of 2.64 Å in the carbide nido-cluster $Fe_5C(CO)_{15}$ (III) [7]. The distances $Fe-C_{int.} = 1.900$ (2) (axial) and 1.884 (1) (equatorial) Å in I correspond to $Fe_{apex}-C = 1.96$ Å and $Fe_{base}-C = 1.90$ Å in III. The distance $Rh-C_{int.} = 2.037$ (1) Å is much smaller than the corresponding distance in the trigonal-pyramidal carbide cluster $[Rh_6C(CO)_{15}]^-$ of 2.134 Å [8], which means that the hole in the metal cluster decreases from a trigonal prism to an octahedron [1]. Due to disorder of the polyhedron in I ("Rh up-Rh down"), the distances M_{ax} –CO (M = Rh, Fe) are not very informative. Rather more important is the fact that the distances $M \cdots C(2)$ decrease to 2.574 (Rh) and 2.558 Å (Fe(1)) accompanied by an apparent distortion

(Continued on p. 144)

TABLE 2

ATOMIC COORDINATES IN I ($\times 10^4$, $\times 10^5$ FOR Rh AND Fe)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	3/4	1/4	20879(10)	4.87(3)	4.86(3)	2.41(4)	0.32(3)	0	0
Fe(1)	3/4	1/4	19482(24)	5.96(7)	5.97(7)	4.3(1)	0.16(6)	0	0
Fe(2)	65325(6)	14036(6)	−692(7)	3.93(3)	3.80(3)	2.91(3)	−0.34(3)	0.09(3)	−0.32(3)
O(1)	8897(3)	1597(3)	4060(4)	6.5(2)	4.8(2)	5.5(2)	0.3(2)	0.5(2)	0.0(2)
O(2)	5897(4)	585(3)	2626(3)	10.3(3)	5.3(2)	2.9(2)	−2.4(2)	0.7(2)	0.3(2)
O(3)	6725(3)	−627(3)	−1362(4)	6.9(2)	4.7(2)	4.4(2)	−0.6(2)	0.6(2)	−1.8(2)
O(4)	4448(3)	1572(3)	−1193(4)	3.9(2)	6.6(2)	6.6(2)	−0.9(2)	−0.6(2)	−0.7(2)
N	1/4	1/4	5135(8)	3.2(2)	3.2(2)	2.9(3)	0	0	0
C	3/4	1/4	0	3.7(3)	3.7(2)	2.0(3)	0	0	0
C(1)	8339(5)	1912(4)	3235(6)	5.1(3)	4.0(3)	5.6(3)	−0.3(2)	1.9(2)	−1.2(2)
C(2)	6211(5)	999(5)	1706(5)	8.1(4)	4.9(3)	3.1(2)	1.2(3)	0.5(3)	−0.8(2)
C(3)	6671(4)	158(4)	−822(5)	4.4(3)	5.3(3)	2.5(2)	−0.7(2)	0.6(2)	−0.2(2)
C(4)	5261(4)	1532(4)	−715(6)	4.2(3)	4.1(3)	3.9(2)	−0.7(2)	0.6(2)	−0.4(2)
C(5)	2985(11)	3307(9)	4163(12)	7.6(8)	4.4(6)	4.7(6)	0.0(6)	1.6(6)	1 2(5)
C(5′)	3299(9)	2005(9)	6100(13)	4.3(6)	5.0(6)	7.3(8)	1.1(5)	−2.1(6)	1.7(6)
C(6)	3504(5)	4191(5)	5138(9)	5.9(3)	3.9(3)	14.2(6)	−1.4(3)	−0.5(4)	1.2(4)

[a] Anisotropic temperature factors are given in the form: $T = \exp(-1/4(B_{11}a^{\star 2}h^2 + B_{22}b^{\star 2}k^2 + B_{33}c^{\star 2}l^2 + 2B_{12}a^{\star}b^{\star}hk + 2B_{13}a^{\star}c^{\star}hl + 2B_{23}b^{\star}c^{\star}kl)$.

TABLE 3

ATOMIC COORDINATES IN II ($\times 10^4$, $\times 10^5$ FOR M)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M(1)	3/4	1/4	20585(6)	1.38(3)	1.38(3)	1.50(3)	−0.30(2)	0	0
M(2)	−18484(3)	37907(3)	140(4)	1.34(2)	1.13(2)	1.72(2)	−0.145(9)	−0.01(1)	0.08(1)
O(1)	−941(3)	3055(3)	4209(4)	2.8(2)	4.2(2)	1.9(1)	−0.5(2)	−0.9(1)	0.3(1)
O(2)	−3225(3)	4678(3)	2319(4)	2.6(2)	2.0(1)	2.2(1)	0.0(1)	0.0(1)	−1.0(1)
O(3)	−121(3)	4531(3)	1733(5)	2.5(2)	3.3(2)	4.1(2)	−1.6(1)	−0.6(1)	0.0(2)
O(4)	−2195(3)	5732(3)	−1519(5)	3.4(2)	2.6(2)	5.4(2)	−0.2(2)	−1.3(2)	1.6(2)
C(1)	−1528(4)	2841(3)	3395(5)	2.0(2)	1.9(2)	1.5(2)	0.0(2)	0.0(2)	0.2(1)
C(2)	−3015(4)	4006(4)	1611(6)	2.7(2)	2.2(2)	2.8(2)	−0.1(2)	−0.2(2)	−0.8(2)
C(3)	−776(4)	4262(4)	1088(5)	2.2(2)	1.4(2)	2.2(2)	−0.2(2)	0.7(2)	0.5(2)
C(4)	−2069(4)	4996(4)	−958(5)	1.6(2)	2.4(2)	2.5(2)	−0.2(2)	−0.1(2)	0.6(2)
N	3/4	3/4	4532(8)	1.6(2)	1.62(2)	1.1(2)	0	0	0
C(5)	−3264(8)	7010(8)	3520(10)	1.8(4)	2.3(4)	2.0(4)	0.0(3)	−0.9(3)	−0.9(3)
C(5)	−2001(8)	6743(7)	5499(10)	2.7(4)	2.0(4)	1.1(3)	0.7(3)	−1.1(3)	0.5(3)
C(6)	−4097(5)	6458(5)	4535(9)	2.0(2)	3.0(3)	6.5(3)	−0.8(2)	0.4(3)	0.0(3)

Anisotropic temperature factors are given in the form: $T = \exp[-1/4(B_{11}a^{\star 2}h^2 + B_{22}b^{\star 2}k^2 + B_{33}c^{\star 2}l^2 + 2B_{12}a^{\star}b^{\star}hk + 2B_{13}a^{\star}c^{\star}hl + 2B_{23}b^{\star}c^{\star}kl)]$.

of the linear coordination Fe(2)-C(2)-O(2) (163.3(5)°) and elongation of the Fe(2)-C(2) bond to 1.855(3) Å as compared with the other two bonds (Fe(2)-C(3) 1.771(5) and Fe(2)-C(4) 1.762(5) Å). Thus four of the 16 CO ligands in the cluster anion I are semi-bridging.

The structure of $[Rh_5Fe(CO)_{16}]^-$ *and comparison with IIa*

Anion II is isostructural with the neutral octahedral cluster $Rh_6(\mu_3\text{-}CO)_4(CO)_{12}$ (IV) [9]. The parameters of the cluster anions in II and IIa [6] and those of IV are compared in Table 5. The M-M distances in the disordered cluster nucleus Rh_5Fe in II and IIa are in good agreement with each other, and the M-C bond lengths are only slightly different. The latter fact may be due either to the disorder which decreases accuracy or to the different crystallographic environments of $[Rh_5Fe(CO)_{16}]^-$ in II and IIa. That the M-M distances are the same in II and IIa but widely different from the Rh-Rh distance in IV is just more evidence in favor of the "disordered" model and, consequently, of the determined cluster II composition (see the Experimental section).

TABLE 4

MOST IMPORTANT GEOMETRICAL PARAMETERS OF I AND II

Bond length (Å)		Angle (°)	
I. $[RhFe_5C(CO)_{16}]^-$			
Rh-Fe(2)	2.823(1)	C(1)RhC(1′)	99.4(3)
Fe(1)-Fe(2)	2.723(2)	C(1)Fe(1)C(1′)	92.8(3)
Fe(2)-Fe(2′)	2.666(1)	C(2)Fe(2)C(3)	98.9(3)
$Rh-C_{intern}$	2.037(1)	C(2)Fe(2)C(4)	98.8(3)
$Fe(1)-C_{intern}$	1.900(2)	C(3)Fe(2)C(4)	91.7(2)
$Fe(2)-C_{intern}$	1.884(1)	RhC(1)O(1)	174.3(5)
Rh-C(1)	1.730(6)	Fe(1)C(1)O(1)	176.0(5)
Rh · · · C(2)	2.574(6)	Fe(2)C(2)O(2)	164.3(5)
Fe(1)-C(1)	1.821(6)	Fe(2)C(3)O(3)	176.3(5)
Fe(1) · · · C(2)	2.558(6)	Fe(2)C(4)O(4)	175.9(5)
Fe(2)-C(2)	1.855(5)		
Fe(2)-C(3)	1.773(5)		
Fe(2)-C(4)	1.762(5)		
C(1)-O(1)	1.152(7)		
C(2)-O(2)	1.120(7)		
C(3)-O(3)	1.142(7)		
C(4)-O(4)	1.147(6)		
II [a]. $[Rh_5Fe(CO)_{16}]^-$			
M(1)-M(2)	2.742(1)	C(1)M(1)C(1′)	95.2(2)
M(2)-M(2′)	2.748(1)	C(2)M(2)C(3)	97.5(2)
M(1)-C(1)	1.875(5)	C(2)M(2)C(4)	96.4(2)
M(1)-C(2)	2.180(6)	C(3)M(2)C(4)	95.5(2)
M(2)-C(2)	2.197(5)	M(1)C(1)O(1)	179.4(5)
M(2′)-C(2)	2.184(5)	M(1)C(2)O(2)	133.5(5)
M(2)-C(3)	1.874(5)	M(2)C(2)O(2)	132 4(5)
M(2)-C(4)	1 886(5)	M(2)C(2)O(2)	134.4(5)
C(1)-O(1)	1.140(6)	M(2)C(3)O(3)	178.8(5)
C(2)-O(2)	1.160(6)	M(2)C(4)O(4)	178.6(5)
C(3)-O(3)	1.131(7)		
C(4)-O(4)	1.135(7)		

[a] M(1) is the metal atom in the axial and M(2) that in the equatorial position.

TABLE 5

MEAN INTERATOMIC DISTANCES (Å) IN THE CLUSTERS $[Rh_5Fe(CO)_{16}]^-$ (II and IIa) AND $Rh_6(CO)_{16}$ (IV)

	II	IIa [6]	IV [9]
M–M	2.745	2.750	2.776
M–C	1.878	1.860	1.864
M–C (μ_3)	2.187	2.175	2.168
C–O	1.135	1.132	1.155
C–O (μ_3)	1.160	1.168	1.201

Ligand environment geometry in I and II

During the investigations of the structure of transition metal carbonyl clusters $M_n(CO)_m$ ($n = 2$ to 6) the existence of certain stable ligand configurations, corresponding to minimum steric interaction energy in the dense coordination sphere of the cluster, has been established. This prompted the conception of a "ligand polyhedron" transferring from one compound to another, in the inner space of which the metal cluster proper is situated [3,10]. In the cluster anions studied here the CO ligands build themselves up into a highly symmetrical 16-vertex polyhedron. Figure 2 is a stereoscopic view of the ligand polyhedron in I which contains in its interior the carbide cluster $RhFe_5(C)$ (the CO ligands are shown by points located at the positions of the C atoms). The arrangement of the CO ligands corresponds to one of the optimum configurations with minimum repulsion between ligands [10]: in Johnson and Benfield's notations the ligand polyhedron is composed of the

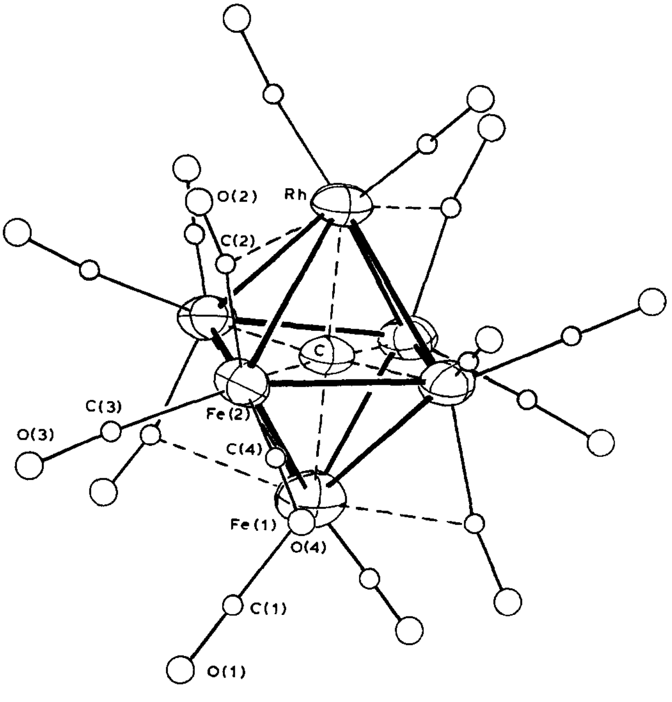

Fig. 1. Cluster anion I.

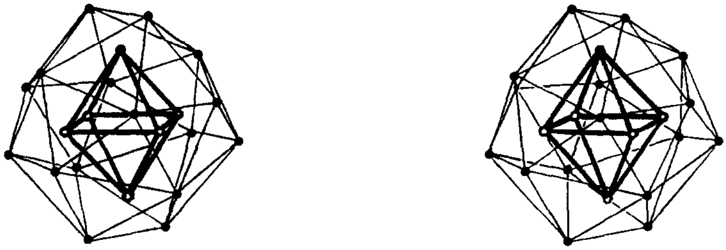

Fig. 2. Cluster I within its ligand polyhedron (stereoview).

Fig. 3. Cluster II within its ligand polyhedron (stereoview).

$1:6:3:(3):3$ layers (Fig. 2). The CO ligand shell in I may, alternatively, be considered as another energetically favorable $4:(4):4:(4)$ configuration distorted due to the bending of the top and bottom 4-ligand "layers". These interpretations are equivalent; in reality, the polyhedron symmetry is close to T_d ($\bar{4}3m$), and the first interpretation corresponds to stratification along the third-order axis, and the second along the $\bar{4}$-axis. In II the configuration of the CO shell is similar (the stereoscopic view is shown in Fig. 3), although the metal polyhedron inside it is rotated by about 45° relative to the octahedron in I, whereby the four semi-bridging CO ligands located over the octahedron edges in I become the face-bridging (μ_3) in II. The lack of stereochemical rigidity of the clusters of this type was attributed to the rotation of the cluster nucleus M_n into the total "coordination field" of the ligand shell [10]. The specific disorder of the M_5M' octahedrons in I and II may serve as indirect evidence of the readiness with which the metal cluster can change its orientation within the ligand polyhedron (cf., also, ref. 11).

References

1 P. Chini, G. Longoni and V.G. Albano, Adv. Organomet. Chem., 14 (1976) 285.
2 B.F.G. Johnson and R.E. Benfield, Topics Stereochem., 12 (1981) 253.
3 B.F.G. Johnson and J. Lewis, Adv. Inorg. Chem. Radiochem., 24 (1981) 225.
4 V.E. Lopatin, N.M. Mikova and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1925.
5 International Tables for X-Ray Crystallography, 4, Kynoch Press, Birmingham, 1974, pp. 71–102.
6 A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni, R. Della Pergola, B.T. Heaton and D.O. Smith, J. Chem. Soc. Chem. Commun., (1982) 886.
7 E.H. Brage, L.F. Dahl, W. Hübel and D.L. Wampler, J. Amer. Chem. Soc., 84 (1962) 4633.
8 V.G. Albano, M. Sansoni, P. Chini and S. Martinengo, J. Chem. Soc. Dalton Trans., (1973) 651.
9 E.R. Corey, L.F. Dahl and W. Beck, J. Amer. Chem. Soc., 85 (1963) 1202.
10 B.F.G. Johnson and R.E. Benfield, J. Chem. Soc. Dalton Trans., (1978) 1554; ibid., (1980) 1743.
11 M.I. Bruce, B.K. Nicholson and A.H. White, J. Organomet. Chem., 240 (1982) C33.