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DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

II *. THE PROTONATION OF η-DIARYLDIENONE(η-CYCLOPENTADIENYL)-RHODIUM(I) AND -IRIDIUM(I) COMPLEXES

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Summary

Reaction of $[M(\eta^4\text{-PhCH=CRCH=CHCOPh})(\eta^5\text{-}C_5H_5)]$, [M = Rh or Ir; R = H or Me] with HBF_4 or HPF_6 affords the crystalline salts $[M(\eta^3\text{-PhCHCRCHCH}_2\text{-COPh})(\eta^5\text{-}C_5H_5)]Y$, [Y = BF_4 or PF_6], in which the acyl CO group is coordinated to the metal. HCl and HBr also protonate the dienone complexes (M = Rh) at carbon, giving the covalent derivatives $[RhX(\eta^3\text{-PhCHCHCHCH}_2\text{COPh})(\eta^5\text{-}C_5H_5)]$, [X = Cl, Br]. A mechanism involving *endo* addition of H^+ to the η^4-dienone ligand is in accord with deuteration studies. ^1H and ^{13}C NMR spectra of the new complexes are discussed. The reactions of $[Rh(\eta^4\text{-PhCHCHCHCHPh})(\eta^5\text{-}C_5H_5)]$ with HCl and HBr are also reported.

Protonation of complexes of the cyclopentadienyl-rhodium(I) and -iridium(I) groups with cyclic olefins such as cyclohexa-1,3-diene [2], cycloocta-1,5-diene [3], cycloocta-1,3,5-triene [4] and cycloocta-1,3,5,7-tetraene [5] has been studied in some detail. In acid media proton exchange in η^4-cyclohexa-1,3-diene(η-cyclopentadienyl)rhodium(I) occurs at the *endo* methylene position of cyclohexadiene via interaction with the metal. Further evidence for *endo* addition of H^+ was obtained from observations on complexes of limonene and α-phellandrene [6]. Carvone(cyclopentadienyl)-rhodium [6] and -iridium [7], however, are protonated at the ketonic oxygen, rather than at carbon.

Reactions of dienetricarbonyliron(0) complexes with a variety of acids including hydrogen chloride, trifluoroacetic acid and fluorosulphonic acid have been summarized [8]. Hydrogen chloride adds to butadienetricarbonyliron at

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* For part I see ref. 1.

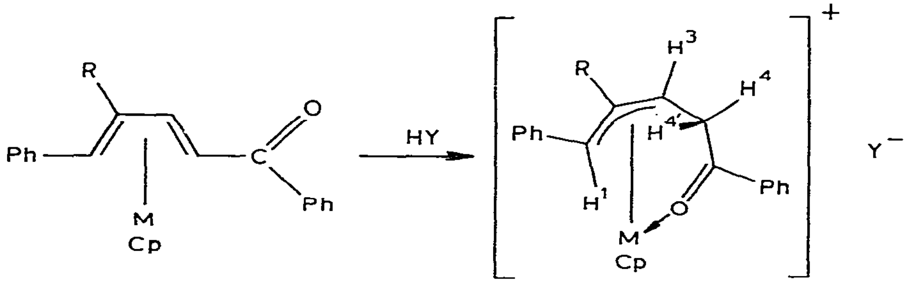
room temperature to give the covalent complex chloro(*syn*-1-methylallyl)tricarbonyliron [9]. Whitesides and Arhart showed that addition of DCl to (1-phenyl-3-methylbutadiene)tricarbonyliron at —78°C occurs stereospecifically to afford a product with an *anti* CH_2D substituent [10]. It is likely therefore that in the reaction of butadienetricarbonyliron the *anti*-1-methylallyl derivative is formed initially but then rearranges to the *syn* isomer.

Studies of hydrogen/deuterium exchange in cyclohexadienetricarbonyliron complement those on the rhodium and iridium complexes, again showing that the addition occurs stereospecifically *endo* [10]. Protonation of η^4-dienonetricarbonyliron complexes, however, by fluorosulphonic acid or by sulphuric acid takes place at the carbonyl oxygen atom to give *trans*-hydroxypentadienyltricarbonyliron cations, which rearrange on warming to 0°C to isomeric *cis*-hydroxypentadienyl cations [11,12]. Cycloheptadienonetricarbonyliron is also protonated at the oxygen of the ketone group [13].

In view of these findings, and to aid the interpretation of some results on protonation of η^4-dienol(η^5-cyclopentadienyl)-rhodium and -iridium complexes, we have studied the reactions of the η^4-dienone compounds I—IV, with acids HY having weakly (Y = CF_3COO, BF_4, PF_6) or strongly (Y = Cl, Br) coordinating anions.

Results and discussion

When a solution of I in $CDCl_3$ is treated with trifluoroacetic acid at —40°C and then allowed to warm to room temperature, a deep orange solution is formed. The ^1H NMR spectrum shows the presence of an η^3-allylic complex, formed by protonation at the terminal carbon atom of the diene system, adjacent to the keto group.



(I , R = H, M = Rh ;
II , R = Me, M = Rh ;
III , R = H, M = Ir ;
IV , R = Me, M = Ir)

(V, R = H, M = Rh, Y = BF_4 ;
VI, R = H, M = Rh, Y = PF_6 ;
VII, R = Me, M = Rh, Y = BF_4 ;
VIII, R = Me, M = Rh, Y = PF_6 ;
IX, R = H, M = Ir, Y = PF_6 ;
X, R = Me, M = Ir, Y = BF_4 ;
XI, R = Me, M = Ir, Y = PF_6)

Similar results are obtained with compounds II—IV. The cations can be isolated

(Continued on p. 234)

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES $[M(\eta^3\text{-PhCHCRCHCH}_2\text{COPh})(C_5H_5)]Y$ AND $[RhX(\eta^3\text{-PhCHCHCHCH}_2Q)(C_5H_5)]$

Complex	Colour	Yield	M.p. θ_c (°C)	Analysis (%) [a]			IR (cm^{-1}) [b] $\nu(CO)$
				C	H	X	
V M = Rh, R = H, Y = BF_4	Orange	50	175 (decomp.)	54.1(53.9)	4.2(4.1)		1570
VI M = Rh, R = H, Y = PF_6	Orange	65	170 (decomp.)	47.8(48.2)	3.8(3.6)		1570
VII M = Rh, R = Me, Y = BF_4	Orange	80	118–119	54.4(54.7)	4.5(4.4)		1575
VIII M = Rh, R = Me, Y = PF_6	Orange	79	150–152 (decomp.)	49.2(49.1)	4.1(3.9)		1575
IX M = Ir, R = H, Y = PF_6	Yellow	87	167–168 (decomp.)	41.5(41.4)	3.3(2.2)		1560
X M = Ir, R = Me, Y = BF_4	Yellow	77	116–118	46.1(46.5)	3.9(3.7)		1565
XI M = Ir, R = Me, Y = PF_6	Yellow	68	148–149	42.4(42.4)	3.5(3.4)		1565
XIII X = Cl, Q = Ph	Maroon	61	129–130	61.4(61.4)	5.0(4.9)		—
XIV X = Br, Q = Ph	Maroon	68	131–132	55.4(55.4)	4.4(4.4)		—
XV X = Cl, Q = COPh	Maroon	75	128–129	60.2(60.2)	4.7(4.6)	8.4(8.1)	1675
XVI X = Br, Q = COPh	Maroon	63	133–134	54.8(54.7)	4.3(4.2)	16.6(16.5)	1675

[a] Calculated values are given in parentheses. [b] Nujol mull.

TABLE 2

HYDROGEN-1 NMR DATA FOR THE COMPLEXES [M(η^3-PhCH^{1}CR^{2}CH^{3}CH^{4}H$^{4'}$COPh)(C$_5$H$_5$)]Y [a] AND [RhX(η^3-PhCH^{1}CH^{2}CH^{3}CH^{4}H$^{4'}$Q)(C$_5$H$_5$)] [b]

Complex	Chemical shift (δ, ppm)						
	H^1	H^2 or R	H^3	H^4	H$^{4'}$	C$_5$H$_5$	Ph resonances
V	4.03(d) J(H^2) 11.6	6.24(m)	6.24(m)	4,28(dd), J(H$^{4'}$) 21, J(H^3) 6.3	3,48(dd), J(H^4) 21, J(H^3) 1.7	5,46(d) J(Rh) 0.9	7.91(d), 7,76(t), 7.55(m) 7,40(m)
VIII	4.00(s)	2,19(d) J(Rh) 1.7	5,99(dd) J(H^2) 8.0 J(Rh) 2,1	4,31(dd) J(H^4) 20.9 J(H^3) 8,2	3,47(dd) J(H^4) 21.0 J(H^3) 2,1	5,53(d) J(Rh) 0.7	7,88(d), 7,74(t), 7,57(m) 7,40(m)
IX	3,44(dd) J(H^2) 10.4 J(?) 0.8	6.74(dd) J(H^1) 11.1 J(H^3) 6.7	5,85(t) J(H^2, H^4)	4,28(dd) J(H$^{4'}$) 21.5 J(H^3) 7.6	3.18(dd) J(H^4) 21.5 J(H^3) 1.5	5,59(s)	7.98(d), 7.79(t), 7.56(t), 7.35(m)
XI	3.54(s)	2,21(s)	5,74 [c]	4,35(dd) J(H$^{4'}$) 21.6 J(H^3) 8.2	3,22(dd) J(H^4) 21.5 J(H^3) 1.6	5.70(s)	7.94(d), 7.76(t), 7.53(m) 7.39(m)
XIII	5.00(d) J(H^2) 12.0	5.54(ddd) J(H^1) 12.0 J(H^3) 7.5 J(Rh) 2.0	5,30(m)	2,54(dd) J(H$^{4'}$) 14.8 J(H^3) 11.0	2.91(dd) J(H^4) 14.8 J(H^3) 3.6	5.15(d) J(Rh) 0.6	7.54(m), 7.31(m)
XIV	5.17(d) J(H^2) 11.8	5.45(ddd) J(H^1) 12.0 J(H^3) 7.3 J(Rh) 2.0	5,24(m)	2.62(dd) J(H$^{4'}$) 14.7 J(H^3) 11.4	3.02(dd) J(H^4) 14.7 J(H^3) 3.5	5.17(d) J(Rh) 0.5	7.54(m), 7.26(m)
XV	4.82(d) J(H^2) 12.1	5.74(ddd) J(H^1) 12.0 J(H^3) 7.7 J(Rh) 1.9	5.50(m)	2.95(dd) J(H$^{4'}$) 18.9 J(H^3) 9.0	3.53(dd) J(H^4) 18.9 J(H^3) 5.2	5.18(d) J(Rh) 0.5	7.94(m), 7.52(m), 7.42(m) 7.26(m)
XVI	5.00(d) J(H^2) 12.1 J(H^2) 12.1	5.66(ddd) J(H^1) 12.1 J(H^3) 7.7 J(H^2) 2.0	5.42(m)	3.09(dd) J(H$^{4'}$) 18.7 J(H^3) 9.2	3.65(dd) J(H^4) 18.7 J(H^3) 5.0	5.21(d) J(Rh) 0.5	7.94(m), 7.52(m), 7.42(m) 7.27(m)
Isomer of XVI	4.94(d) J(H^2) 10.6	5.84(ddd) J(H^1) 10.6 J(H^3) 8.0	4.73(m)	4.39(dd) J(H$^{4'}$) 18.1 J(H^3) 7.8	3.87(dd) J(H^4) 18.1 J(H^3) 4.4	5.32(d) J(Rh) 0.5	

[a] Measured in CD$_2$Cl$_2$ relative to tetramethylsilane, δ = 0 ppm. Coupling constants in Hz. [b] Measured in CDCl$_3$. [c] Signal obscured by cyclopentadienyl resonance.

TABLE 3

CARBON-13 NMR DATA [a] FOR COMPLEXES $[MPhC^1HC^2RC^3HC^4H_2C^5(O)Ph(C_5H_5)]Y$

Complex				δ (ppm)							
	M	R	Y	C^1	C^2	C^3	C^4	C^5	R	C_5H_5	Ph
V	Rh	H	BF_4	87.5 (8.0)	89.2 [b]	72.6 (10.6)	44.7	221.5	—	89.5 (6.6)	140.6, 137.6, 134.2, 131.3, 130.4, 129.5, 127.8
VII	Rh	Me	BF_4	89.0 (8.0)	110.2 (5.3)	73.7 (10.6)	46.0	221.6	22.4	90.2 (6.6)	139.5, 137.6, 134.2, 131.3, 131.1, 130.4 129.7 128.9
IX	Ir	H	PF_6	74.7	81.4	58.1	44.8	226.7	—	83.3	141.8, 138.3, 134.2, 132.0, 130.8, 130.5, 128.8, 127.4
X	Ir	Me	BF_4	77.1	102.6	60.3	45.9	226.4	23.9	83.8	140.1, 138.0, 134.0, 131.9, 131.3, 130.7, 129.8, 128.4

[a] Measured in CD_3NO_2. Chemical shifts (δ) in ppm relative to $SiMe_4$, positive values to high frequency. J(RhC) in Hz given in parentheses. [b] Partially obscured by cyclopentadienyl resonance.

as air stable, crystalline tetrafluoroborates or hexafluorophosphates (V—XI), either by addition of the solution in $CHCl_3/CF_3COOH$ to HBF_4 in diethyl ether or, usually in better yield, by treatment of the dienone complex directly with $HPF_6 \cdot Et_2O$ in ether (Table 1).

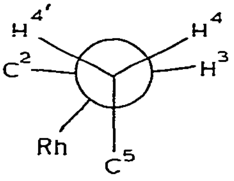
The structure of the protonated complexes is proposed largely on the basis of NMR results (Tables 2 and 3). Off-centre double resonance carbon-13 spectra of the salts V, VII, IX and X all showed a triplet at about 45 ppm, indicating the presence of a methylene group. This is not immediately apparent from the hydrogen-1 spectra as protons H^4 and $H^{4'}$ are magnetically inequivalent, C^4 lying adjacent to a chiral centre at C^3.

Structural evidence will be discussed mainly with reference to compound IX. In this case the assignments of the proton resonances were aided by detailed double resonance experiments; those of the carbon-13 peaks were confirmed by selective irradiation at appropriate resonant frequencies in the proton spectrum.

The coupling constant $J(H^1H^2) = 10.4$ Hz is typical of a *trans* coupling in iridium complexes, while $J(H^2H^3) = 6.7$ Hz indicates a *cis* arrangement of the hydrogens. This places the 1-phenyl substituent *syn* and the 3-$PhCOCH_2$ substituent *anti* with respect to the allyl group. The η^3-allyl structure is further supported by the observation of coupling between ^{103}Rh and the protons of the 2-methyl group in the spectrum of VIII. Similar couplings are found in 2-methylallylrhodium complexes [14]. Moreover the carbon-13 spectra of V and VII show Rh—C couplings only to C^1, C^2 and C^3, but not to C^4 or C^5. The coupling constant $J(RhC^2) = 5.3$ Hz is lower than those to C^1 or C^3, in agreement with previous findings [15].

The structure proposed for compounds V—XI is similar to that found in the intermediate isolated from Friedel Crafts acylation of dienetricarbonyliron complexes [16]. An X-ray diffraction study of one such intermediate, tricarbonyl-(1-3-η-hexen-5-one)iron hexafluorophosphate, showed that the oxygen atom of the ligand is coordinated to iron, so that the 18-electron configuration of the metal is preserved [17]. The acyl CO stretching frequency in this compound is lowered to 1637 cm^{-1}. We also observe a considerable lowering of $\nu(CO)$ in our products. In the precursor dienone complex I, $\nu(CO)$ falls at 1650 cm^{-1}, while in the infrared spectrum of V there are two peaks at 1600 cm^{-1} and 1570 cm^{-1}, the second of which being broader and more intense, is assigned to $\nu(CO)$, the other probably being due to aromatic vibrations. We therefore deduce that the acyl oxygen is also coordinated to the metal in complexes V—XI. This coordination restricts rotation about the C^3—C^4 bond. The presence of a chiral centre at C^3 makes the two protons H^4, $H^{4'}$ of the adjacent CH_2 group magnetically inequivalent. The conformation of substituents about the C^3—C^4 bond is shown below, looking from C^4 towards C^3.

(D)



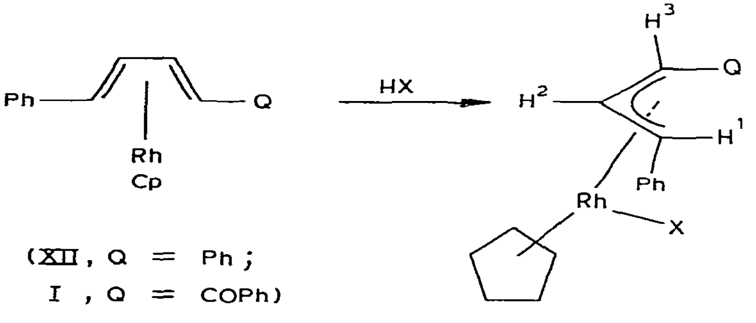
The hydrogen-1 NMR spectra of V—XI are characterised by a) a large geminal coupling constant $J(H^4H^{4'})$ of about 21 Hz. b) one very small vicinal coupling of ca. 2 Hz to the higher field proton of the C^4H_2 pair. c) a vicinal coupling of ca. 8 Hz to the lower field proton of the C^4H_2 group.

A small vicinal coupling constant indicates a dihedral angle of about 90° between the planes C^4—C^3—H^3 and C^3—C^4-$H^{4'}$ [18]. This angle is 98° in tricarbonyl(1-3-η-hexen-5-one)iron hexafluorophosphate, corresponding to a coupling constant of 2 Hz [19]. This identifies the higher field resonance with $H^{4'}$, which is also the proton which lies nearer to the metal centre (high field shift).

Deuteriation of I—IV gives spectra in which the higher field resonance is absent. Addition of H^+ or D^+ is thus stereospecific and, as shown above, must occur from the *endo* side of the diene, possibly via a metal hydride. No intermediate metal hydride, however, was detected under the experimental conditions used.

Treatment of (η^4-1,3-diphenylbuta-1,3-diene)(η-cyclopentadienyl)rhodium [20] (XII) with hydrogen chloride or hydrogen bromide in ether affords the complexes XIII and XIV in fair yield. Their proton NMR spectra generally resemble those of V—XI. The resonance assigned to H^1 is at rather lower field than usual for an *anti*-H substituent, although there are precedents [21]. The value of $J(H^1H^2) = 12$ Hz, however, is consistent with *trans* coupling. H^4 and $H^{4'}$ are again magnetically inequivalent. It has been suggested that such marked inequivalence is characteristic of an *anti* CH_2R substituent [22].

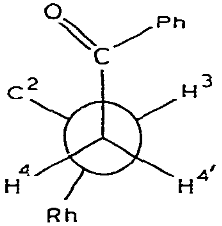
The dienone complex I likewise yields deep maroon air stable derivatives XV and XVI with hydrogen chloride and hydrogen bromide, respectively. The infrared spectra of XV and XVI show a strong band at 1675 cm^{-1}, which is assigned to ν(CO). Coordination of the acyl carbonyl group to rhodium therefore does not occur here: the metal attains an 18-electron configuration by bonding to chlorine.



(XII, Q = Ph;
I, Q = COPh)

(XIII, Q = Ph, X = Cl;
XIV, Q = Ph, X = Br;
XV, Q = COPh, X = Cl;
XVI, Q = COPh, X = Br)

Whereas in the hydrogen-1 NMR spectra of compounds V—XI the higher field resonance of the H^4, $H^{4'}$ pair is associated with the smaller coupling to H^3, for compounds XIII—XVI it is the resonance at lower field. If the carbonyl group is not coordinated to the metal (compounds XV, XVI) or is absent (compounds XIII, XIV), rotation about the C^3—C^4 bond will no longer be restricted. The NMR spectra should therefore be discussed with reference to the favoured conformation about the C^3—C^4 bond. The proton which lies nearer to the metal (H^4) would be expected to resonate at higher field, and also to couple more strongly to H^3 (dihedral angle approaches 180°). That further from the metal centre ($H^{4'}$) will appear at lower field and couple less strongly to H^3 (dihedral angle ~60°). Stereospecific *endo* addition is again indicated by deuteriation with DBr; the lower field resonance is identified with $H^{4'}$.



(D)

Although excellent elemental analyses were obtained for XV and XVI, the NMR spectra revealed in each case, in addition to the major component, about 5—10% of another very similar, probably isomeric compound. This might be a conformational isomer, as found for [FeX(η^3-allyl)(CO)$_3$] [23], but such conformational equilibria have not been observed previously for complexes of the type [MX(η^3-allyl)(C_5H_5)] (M = Co [24], or Rh [14,15]). The spectra of XIII and XIV, however, show the presence of only one species. It is tentatively suggested that the minor component may be an isomer of XVI with a *syn* CH_2COPh substituent.

Experimental

Reactions were carried out under dry nitrogen. All the compounds described in this paper, however, appear to be stable to air both in the solid state and in solution. Microanalyses were by Butterworth Laboratories Ltd. Infrared spectra were determined in Nujol mulls using a Perkin-Elmer 257 spectrometer and were calibrated by polystyrene film. Hydrogen-1 (250 MHz) and carbon-13 (68.25 MHz) NMR spectra were recorded on a Bruker spectrometer at King's College, London. (η^4-Diphenylbutadiene)(η^5-cyclopentadienyl)rhodium was prepared by a modification of the literature method [20]. The general procedure for making the dienone complexes I—IV has been described previously [1].

Reaction of [M(dienone)(C_5H_5)], I—IV, with hexafluorophosphoric acid

A typical reaction is described. Compound I (0.26 g) in diethylether (70 cm³) was cooled to —10°C and $HPF_6 \cdot Et_2O$ (0.1 cm³) was added with stirring. The reaction mixture was allowed to warm up to room temperature over 1 h. The orange precipitate was filtered off, washed with ether and purified by dissolving in nitromethane, filtering and reprecipitating with ether. Yield 0.232 g (65%).

Reaction of [M(dienone)(C_5H_5)], I—IV, with trifluoroacetic acid followed by tetrafluoroboric acid

A typical reaction is described. The ketone I (0.28 g) was dissolved in chloroform (10 cm^3) and trifluoroacetic acid (0.2 cm^3) added. After stirring for 10 min, the solution was poured into diethyl ether (70 cm^3) which contained tetrafluoroboric acid (0.5 cm^3, 42% aqueous HBF_4). The orange precipitate was filtered, washed with ether and recrystallised from nitromethane/ether. Yield 0.17 g (50%).

Reaction of [Rh(η^4-PhCH=CHCH=CHCOPh)(C_5H_5)] with hydrogen chloride

The ketone I (0.383 g) suspended in diethyl ether (50 cm^3) was treated with concentrated aqueous hydrochloric acid (0.1 cm^3) and the mixture stirred for 1½ h. The complex dissolved to give a deep red solution from which maroon feathery crystals suddenly separated. The product was filtered off, washed with ether, dissolved in dichloromethane (10 cm^3) and refiltered. On addition of petroleum ether (100 cm^3) b.p. 60—80°C) and cooling to —5°C overnight, the product XV (0.314 g, 75%) was obtained as deep maroon crystals.

Complexes XIII, XIV and XVI were prepared similarly.

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References

1 P. Powell and L.J. Russell, J. Chem. Research, (1978) (S) 283, (M) 3652.
2 B.F.G. Johnson, J. Lewis and D.J. Yarrow, J. Chem. Soc. Dalton, (1972) 2084.
3 J. Evans, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton, (1977) 510.
4 J. Evans, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton, (1972) 2668.
5 J. Evans, B.F.G. Johnson, J. Lewis and D.J. Yarrow, J. Chem. Soc., Dalton, (1974) 2375.
6 B.F.G. Johnson, J. Lewis and D.J. Yarrow, J. Chem. Soc., Dalton, (1974) 1054.
7 L.A. Oro, J. Less Common Metals, 53 (1977) 289.
8 M. Brookhart, T.H. Whitesides and J.M. Crockett, Inorg. Chem., 15 (1976) 1550.
9 F.J. Impastato and K.G. Ihrman, J. Amer. Chem. Soc., 83 (1961) 3726; G.F. Emerson, J.E. Mahler and R. Pettit, Chem. Ind. (London), (1964) 836.
10 T.W. Whitesides and R.W. Arhart, J. Amer. Chem. Soc., 93 (1971) 5296.
11 N.A. Clinton and C.P. Lillya, J. Amer. Chem. Soc., 92 (1970) 3065; C.P. Lillya and R.A. Sahatjian, J. Organometal. Chem., 32 (1971) 371.
12 M. Brookhart and D.L. Harris, J. Organometal. Chem., 42 (1972) 441.
13 D.F. Hunt, G.C. Farrant and G.T. Rodeheaver, J. Organometal. Chem., 38 (1972) 349.
14 J. Powell and B.L. Shaw, J. Chem. Soc. (A)., (1968) 583.
15 P. Powell and L.J. Russell, J. Organometal. Chem., 129 (1977) 415.
16 E.O. Greaves, G.R. Knox and P.L. Pauson, Chem. Commun., (1969) 1124.
17 A.D.U. Hardy and G.A. Sim, J. Chem. Soc., Dalton, (1972) 2305.
18 L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd Edn., Pergamon Press, Oxford, 1969.
19 E.O. Greaves, G.R. Know, P.L. Pauson, S. Toma, G.A. Sim and D.I. Woodhouse, J. Chem. Soc. Chem. Commun., (1974) 257.
20 S.M. Nelson, M. Sloan and M.G.B. Drew, J. Chem. Soc., Dalton, (1973) 2195.
21 N.M. Boag, M. Green, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton, (1980) 1200.
22 O.G. Levanda, G.Yu Pek and I.I. Moiseev, Zhur. Org. Khim., 7 (1971) 217.
23 T. Aviles and M.L.H. Green, J. Chem. Soc., Dalton, (1979) 1116.