Journal of Organometallic Chemistry, 134 (1977) 319—325

PENTAMETHYLCYCLOPENTADIENYL-RHODIUM AND-IRIDIUM COMPLEXES

XIV *. THE SOLVOLYSIS OF COORDINATED ACETONE SOLVENT SPECIES TO TRIS(μ-DIFLUOROPHOSPHATO)BIS[η^5-PENTAMETHYLCYCLOPENTADIENYLRHODIUM(III)] HEXAFLUOROPHOSPHATE, TO THE η^5-(2,4-DIMETHYL-1-OXAPENTA-1,3-DIENYL)(PENTAMETHYLCYCLOPENTADIENYL)IRIDIUM CATION, OR TO THE η^5-(2-HYDROXY-4-METHYLPENTADIENYL)(η^5-PENTAMETHYLCYCLOPENTADIENYL)IRIDIUM CATION

COLIN WHITE, STEPHEN J. THOMPSON and PETER M. MAITLIS *

Department of Chemistry, The University, Sheffield S3 7HF (Great Britain)

(Received February 9th, 1977)

Summary

Reaction of $[M(\eta^5\text{-}C_5Me_5)Cl_2]_2$ with $AgPF_6$ in acetone gave $[M(\eta^5\text{-}C_5Me_5)(Me_2CO)_3][PF_6]_2$ (Ia, M = Rh; Ib, M = Ir). Heating an acetone solution of Ia gave $[\{Rh(\eta^5\text{-}C_5Me_5)\}_2(PO_2F_2)_3]PF_6$ (IIa). Heating an acetone solution of Ib gave the η^5-(2-hydroxy-4-methylpentadienyl)(η^5-pentamethylcyclopentadienyl)iridium cation; an intermediate in this reaction, the η^5-(2,4-dimethyl-1-oxapentadienyl)(η^5-pentamethylcyclopentadienyl)iridium cation could also be prepared from Ib and mesityl oxide. Possible reaction mechanisms are discussed.

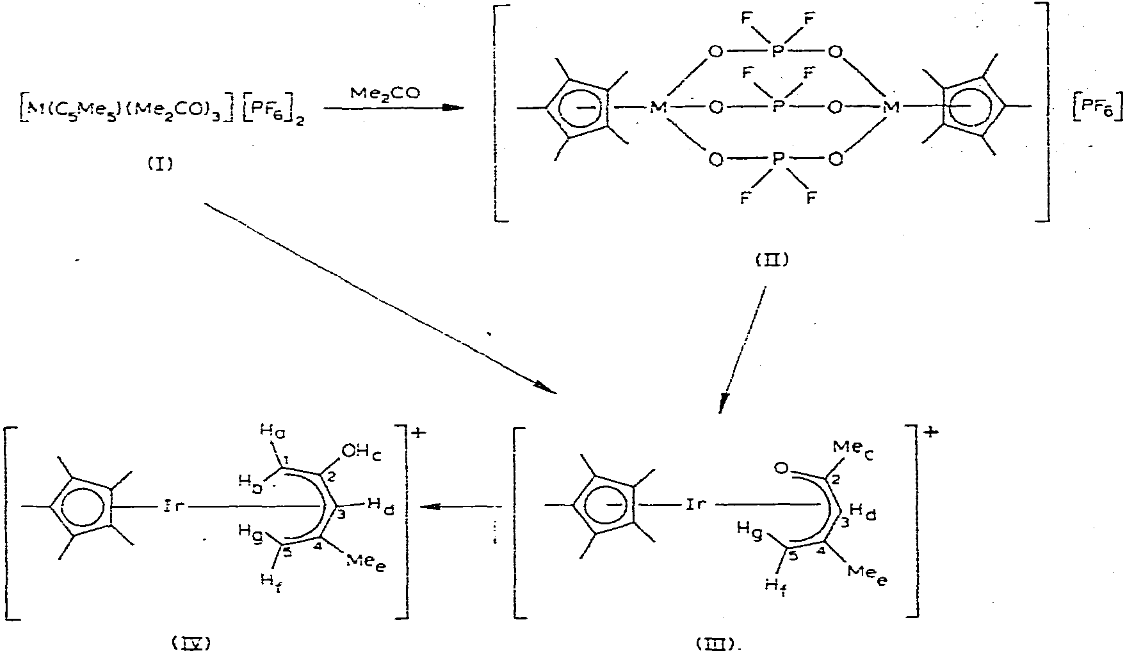
We have recently discussed [2] the dicationic pentamethylcyclopentadienylrhodium and -iridium tris-solvent complexes, $[M(C_5Me_5)(s)_3]^{2+}$ (s = MeCN, Me_2SO, pyridine); the complexes with s = MeCN or Me_2SO are appreciably labile and may be utilised in the synthesis of a variety of derivatives by replacement of solvent by hydrocarbon ligands.

The most useful for this purpose are, however, the acetone species. $[M(C_5Me_5)(Me_2CO)_3][PF_6]_2$ (Ia, M = Rh; Ib, M = Ir) since they are the most labile. However, when attempts were made to isolate them decomposition always occurred and therefore the stoichiometries and structures of these species are uncertain; we write them as tris-acetone complexes by analogy to the isolated and characterised MeCN, Me_2SO, or pyridine complexes.

---

* For part XIII see ref. 1.

The decomposition products of these reactions have, however, been characterised. When the rhodium complex (Ia) in acetone solution was heated (54°C/18 h) an interesting reaction took place in which the PF_6^- ion was partially solvolysed to $PO_2F_2^-$ and the final product contained three such ligands coordinated in a bridging manner to two $Rh(C_5Me_5)$ units. By a combination of X-ray crystallography, and ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy structure IIa was elucidated for the complex [3].



Results and discussions

Tris(μ-difluorophosphato)bis[η⁵-pentamethylcyclopentadienylrhodium(III)] hexafluorophosphate (IIa)

When the decomposition of Ia in acetone-d_6 was followed by ^1H NMR spectroscopy the C_5Me_5 signal at δ 1.79 ppm was slowly replaced by another at δ 1.65 ppm. Further heating caused no further changes, and an orange complex could be isolated from the solution which showed only the presence of a C_5Me_5 group in both the ^1H and the ^{13}C NMR spectra. The IR spectrum showed a very strong band at 835 cm^{-1}, assigned to $\nu(P-F)$ in PF_6^-, as well as strong bands at 1306 and 1135 [$\nu(P=O)$] and 851 and 863 [$\nu(P-F)$] cm^{-1} which are assigned to PO_2F_2. The ^{19}F NMR spectrum showed two doublets (δ +80.4 ppm ($J(F-P)$ 1030 ± 110 Hz) and +71.3($J(F-P)$ 750 ± 80 Hz); CF_3CO_2H as external reference) in a 1/1 ratio. The doublet at +71.3 is in the region, and has a coupling constant of the magnitude, expected for PF_6^- [4]. The chemical shift of the other doublet was consistent with $PO_2F_2^-$; the doublet was broad at +35°C and was unchanged down to −80°C. The presence of a PF_6^- and of three PO_2F_2 groups was confirmed by the ^{31}P NMR spectrum which showed a septet and a triplet (δ −166.2 ppm,

J(P—F) 708 Hz, and −33.2 ppm, J(P—F) 952 Hz; acetone-d_6 solution, H_3PO_4 as external reference) in the ratio of 1/3. The coupling J(P—F) of 952 Hz is close to the literature values of 966 or 980 Hz for $PF_2O(OH)$ [5], but again these resonances were broad. On cooling this sample to −90°C the PF_6^- resonance remained unchanged but the PO_2F_2 resonance was now split into three triplets (δ −34.6 (J 959 Hz), −33.3 (J 955 Hz) and −36.9 ppm (J 952 Hz)) with intensities approximately in the ratio 1/5/6. An exchange process, presumably involving Rh—O bond cleavage, is occurring at ambient temperature. The complex low temperature spectrum may arise from long-range P—F coupling or alternatively the three PO_2F_2 ligands may not all be in the same environment in the frozen-out form. Some support for the latter possibility comes from the X-ray crystal structure determination which indicates some of the PO_2F_2 fluorines in IIa to be disordered [3].

Surprisingly, addition of water to an acetone solution of Ia did not accelerate the reaction, but addition of mesityl oxide increased the rate of formation of IIa by a factor of ca. 15 and the reaction was complete within one hour at 50°C. The complex could also, and more conveniently, be synthesised by reaction of Ia with HPO_2F_2.

The PF_6^- ion has long been regarded as very stable. Lange, who first prepared it, reported that molten caustic alkali was required to break it up (to give fluoride and phosphate) [6], and Ryss and Tul'chinskii later showed that the larger alkali metal ions catalyse this decomposition under alkaline conditions [7].

Hydrolysis to phosphate in 6 M HCl is faster than alkaline hydrolysis but is still very slow and catalysis by highly charged cations (thorium(IV), zirconium(IV), aluminium(III)) has been observed [8,9]. The product of hydrolysis is always phosphate but in the aluminium(III)-catalysed reactions at low acidity kinetic evidence was presented in favour of the build-up of an intermediate, believed to be $PO_2F_2^-$.

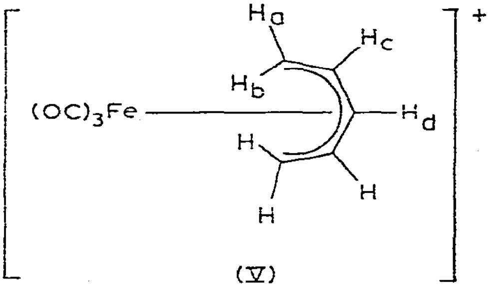
The present work therefore describes the first definitive example of the partial hydrolysis of PF_6^- to $PO_2F_2^-$ and also the first well-defined transition metal complex of the PO_2F_2 ligand, in this case bridging two rhodium atoms.

Rearrangement of $[Ir(C_5Me_5)(Me_2CO)_3][PF_6]_2$ (Ib)

When the iridium acetone solvent complex Ib was allowed to stand in acetone solution at 35°C a series of rearrangements occurred, which could be followed by ^{1}H NMR spectroscopy. The C_5Me_5 singlet due to Ib at δ 1.79 ppm was slowly replaced by another at δ 1.54 ppm which in turn was replaced by yet a third singlet at δ 2.02 ppm; this was the only C_5Me_5 peak remaining after 21 days at 35°C or 3 days at 50°C.

Although it was never possible to isolate the complex, the peak at δ 1.54 ppm is presumed to be due to the iridium difluorophosphate complex IIb. The final product (C_5Me_5 resonance at δ 2.02 ppm) was isolated as colourless crystals showing a peak at 3400 cm^{-1} in the infrared, assigned to ν(OH), which disappeared on exchange with D_2O. Analytical data on various samples of this material were not consistent, the IR spectrum showed no peak in the 830—840 cm^{-1} region so characteristic of the PF_6^- ion, and the ^{19}F NMR spectrum also showed no resonance characteristic of the PF_6^- ion but it did show a singlet (F^-) and some minor peaks. Clearly then this cation was associated with F^- and other anions from the solvolysis of the PF_6^- ion.

This material was converted into the tetraphenylborate salt, $[Ir(C_5Me_5)(C_6H_9O)]BPh_4$, the ^1H and ^{13}C NMR spectra of which were identical (except for the phenyl protons of the BPh_4^- anion) to that of the salt isolated from the initial reaction. Structure IV is assigned to this complex based on the NMR spectra * (^1H, δ (ppm) at 1.38 [d, H_b or H_g, $J(H_b—H_a)$ or $J(H_g—H_f)$ 4 Hz], 1.64 [d, H_g or H_b, $J(H_g—H_f)$ or $J(H_b—H_a)$ 6 Hz] 1.98 (s, C_5Me_5), 2.10 (s, Me_e), 3.26 (d, H_a or H_f, J 4 Hz), 3.50 (dd, H_f or H_a, J 6, 1 Hz), 6.20 (s, broad, OH_c), 6.30 (s, H) and 6.6—7.0 and 7.2—7.4 (mm, BPh_4^-); ^{13}C, δ at 8.9 (C_5Me_5), 23.2 [Me_e] 35.7, 44.7 [C(1), C(5)], 86.1 [C(3)], 96.8 [C_5Me_5], 97.2 [C(2)], 132.5 [C(4)], 122.7, 125.9, 128.1, and 136.9 [phenyls of BPh_4^-]). For comparison, the ^1H spectrum of the pentadienyl(tricarbonyl)iron cation (V) shows H_a at δ 3.75, H_b at 2.17 and H_d at 7.22 ppm with $J(H_a—H_b)$ 3.5, $J(H_a—H_d)$ 1.5 and $J(H_b—H_d)$ 0 Hz [10].



(V)

Since the 2-hydroxy-4-methylpentadienyl ligand in IV is simply the deprotonated enol form $[CH_2\cdots CMe\cdots CH\cdots C(OH)\cdots CH_2]$ of mesityl oxide $[CH_3C(Me)=CHCOCH_3]$, the complex was synthesised by treatment of the acetone solvent complex Ib with mesityl oxide.

In fact, this reaction did not initially give IV but it gave instead an isomer III thereof which was then slowly converted into IV in the presence of acid (HPO_2F_2 or CF_3CO_2H). Complex III as the hexafluorophosphate salt was identified by spectroscopy (^1H NMR, δ (ppm) at 2.00 (s, C_5Me_5); 2.00, 2.41 (ss, Me_c, Me_e), 3.09 (d, H_g, $J(H_g—H_f)$ 3 Hz), 4.19 (d, H_f, J 3 Hz), 6.55 (s, H_d); ^{13}C {^1H}NMR δ at 9.2 (C_5Me_5), 21.8, 23.2 (Me_c, Me_e), 60.3 [C(5)], 86.2 [C(3)], 96.6 [C_5Me_5], 111.7 [C(4)], 157.2 [C(2)]). The IR spectrum showed the presence of PF_6^- (840 cm^{-1}) and the absence of bands that could be ascribed to ν(OH) or free ν(C=O), but it did show a strong band at 1475 cm^{-1} which we assign to coordinated ν(C$\cdots$O), probably coupled to other modes.

Mechanism of the formation of the oxapentadienyl and the hydroxypentadienyl ligands

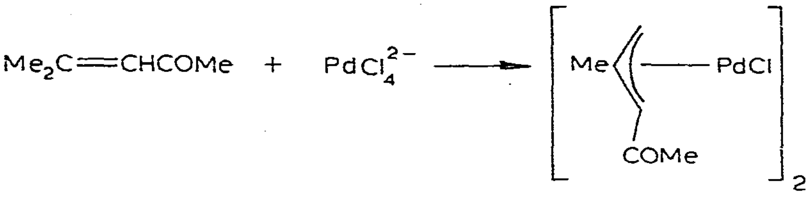
Three separate unusual reactions occur: (i) the selective solvolysis of PF_6^- to coordinated $PO_2F_2^-$, (ii) the deprotonation of mesityl oxide to the oxapentadienyl ligand, and (iii) the isomerisation of the oxapentadienyl ligand to the hydroxypentadienyl ligand.

---

* The spectra of III and IV were assigned on the basis of H—H and selective C—H decoupling experiments.

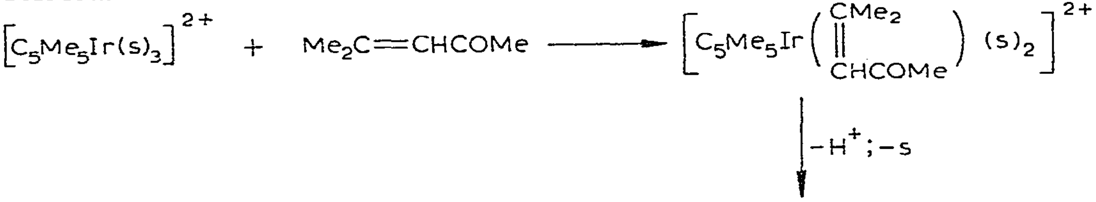
(i) Separate experiments showed that mesityl oxide by itself does not solvolyse the PF_6^- ion in NH_4PF_6; therefore the initial formation of the PO_2F_2 complexes (II) must arise from the combined effect of the metals and mesityl oxide, since water apparently plays no major role. The slowness of the formation of IIa further suggests that the mesityl oxide is being formed in situ by a catalysed aldol condensation.

(ii) The deprotonation of mesityl oxide to form the η^3-allylpalladium complex VI is well-established [11]; the observation of ν(CO) at 1690 cm^{-1} in VI indicated the η^3-mode of bonding and that the carbonyl was not coordinated.



(VI)

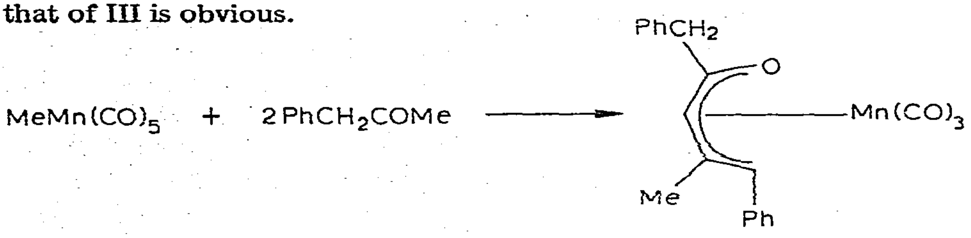
Clearly a similar deprotonation is induced in the reaction of the highly charged Ib with mesityl oxide but the tendency of iridium(III) in these complexes to favour η^5-bonding is so high that the carbonyl is also coordinated and III is formed.



(III)

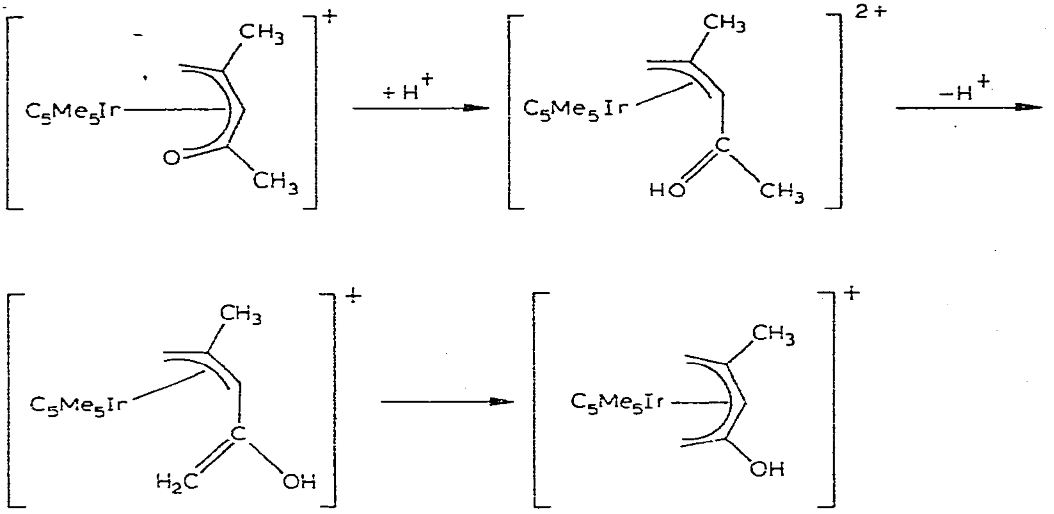
We have no direct proof that III is an intermediate in the formation of IV in the thermal decomposition of an acetone solution of Ib, since the closeness of the positions of the C_5Me_5 resonances of III and IV in the ^{1}H NMR spectra of the reaction mixture makes it impossible to distinguish between them. However, we incline to the view that III is always intermediate in the formation of IV, particularly since the acid generated in the formation of III (as well as any HPO_2F_2 present) would promote the isomerisation III → IV.

Whether indeed we are dealing with a metal-catalysed aldol condensation is not known; certainly such processes have been described [12] and recently Bennett and Bruce [13] obtained a 9% yield of VII by the reaction of two molecules of 1-phenylpropan-2-one with methyl(pentacarbonyl)manganese, methane presumably being eliminated. The analogy between the structure of VII and that of III is obvious.



(VII)

(iii) The acid catalysed isomerisation III → IV is more unusual. The driving force is probably the relative "softness" of the iridium(III) centre [2,3] which encourages the formation of the thermodynamically favoured all-carbon-bonded η^5-pentadienyl over the carbon-and-oxygen-bonded η^5-oxapentadienyl ligand. The mechanism may be envisaged to proceed by an initial decomplexation and protonation of the carbonyl group, and elimination of H^+ from the adjacent methyl (giving the enol form) followed by rotation about the C—C bond and recomplexation. Solvent or anions may well participate. A related isomerisation of the (*syn*-1-*anti*-5-dimethylpentadienyl)(tricarbonyl)iron cation to the *syn*,*syn*-1,5-dimethyl isomer has been reported [14].



Experimental

All reactions were carried out under dry nitrogen.

Tris(μ-difluorophosphate)bis[η^5-pentamethylcyclopentadienylrhodium(III)] hexafluorophosphate (IIa)

Silver hexafluorophosphate (0.5 g, 2.0 mmol) was added to a stirred solution of $[Rh(C_5Me_5)Cl_2]_2$ (0.3 g, 0.5 mmol) in acetone (10 ml). An immediate exothermic reaction occurred to give a white precipitate of silver chloride and an orange solution containing $[Rh(C_5Me_5)(Me_2CO)_3][PF_6]_2$. The silver chloride was removed by centrifugation followed by decantation, and any residual silver salts in the solution were removed by filtering the solution through a short column of powdered cellulose. The solution was made up to 50 ml with more acetone and degassed on a vacuum line by repeatedly freezing and evacuating. Nitrogen was then admitted and the solution was heated at 54°C for 18 h. The solution was then filtered and the solvent removed in vacuo; the crude yellow-orange $[\{Rh(C_5Me_5)\}_2(PO_2F_2)_3]PF_6$ (IIa) (0.45 g, 65%) was crystallised from dichloromethane/ether to give the pure complex (0.12 g). (Found: C, 26.2; H, 3.5. $C_{20}H_{30}F_{12}O_6P_4Rh_2$ calcd.: C, 26.0; H, 3.3%). ^1H NMR at δ 1.65 ppm (s, C_5Me_5); $^{13}C\{^1H\}$ NMR at δ 8.7 (s, C_5Me_5) and 94.7 ppm (d, C_5Me_5, $J(C—Rh)$ 2.5 Hz).

η^5-(2,4-Dimethyl-1-oxapenta-1,3-dienyl)(pentamethylcyclopentadienyl)iridium hexafluorophosphate (III)

Mesityl oxide (0.06 g, 0.6 mmol) was added to a solution containing $[Ir(C_5Me_5)(Me_2CO)_3][PF_6]_2$ (prepared from $[Ir(C_5Me_5)Cl_2]_2$ (0.2 g, 0.25 mmol) and $AgPF_6$ (0.25 g, 1 mmol) in acetone); the solution was heated with stirring (50°C/30 min) and the solvent was then removed in vacuo. The residue was washed with ether to remove any traces of mesityl oxide and then crystallised from chloroform/ether to give the white $[Ir(C_5Me_5)(Me_2C_4H_3O)]PF_6$ (III, 0.16 g, 64%). (Found: C, 34.0; H, 4.2. $C_{16}H_{24}F_6IrOP$ calcd.: C, 33.7; H, 4.4%).

η^5-(2-Hydroxy-4-methylpentadienyl)(η^5-pentamethylcyclopentadienyl)iridium tetraphenylborate (IV)

A solution containing $[Ir(C_5Me_5)(Me_2CO)_3][PF_6]_2$ was prepared as described above from $[Ir(C_5Me_5)Cl_2]_2$ (0.3 g, 0.4 mmol) and $AgPF_6$ (0.4 g, 1.6 mmol) in acetone. The solution was then made up to 30 ml with more acetone and was carefully deoxygenated with nitrogen before being heated (50°C/72 h). The solvent was then removed in vacuo and the residual gum extracted with chloroform; the chloroform was then removed in vacuo and the remaining solid crystallised from dichloromethane/ether to give a white solid (0.12 g) containing the $[Ir(C_5Me_5)\{(2\text{-}HO)(4\text{-}Me)C_5H_5\}]$ cation. This solid was dissolved in acetone and treated with a saturated acetone solution of sodium tetraphenylborate. The acetone was removed in vacuo, excess $NaBPh_4$ removed by washing with cold water and dried to give $[Ir(C_5Me_5)\{(2\text{-}HO)(2\text{-}Me)C_5H_5\}]BPh_4$ (IV) (0.14 g, 32%). (Found: C, 64.2; H, 6.2. $C_{40}H_{44}BIrO$ calcd.: C, 64.6; H, 6.0%).

Acknowledgments

We thank the Science Research Council for support of this work, I.C.I. Ltd., for a grant towards the purchase of chemicals, Professor R. Schmutzler for a gift of difluorophosphoric acid and Mr. Alan Yates for experimental assistance.

References

1 C. White, S.J. Thompson and P.M. Maitlis, J. Organometal. Chem., 127 (1977) 415.
2 C. White, S.J. Thompson and P.M. Maitlis, J. Chem. Soc. Dalton, submitted for publication.
3 S.J. Thompson, P.M. Bailey, C. White and P.M. Maitlis, Angew. Chem. Int. Ed., 15 (1976) 490.
4 J.W. Emsley and L. Phillips, Progr. Nucl. Magn. Reson. Spectrosc., 7 (1971) 474, 475.
5 V. Mark, C.H. Dungan, M.M. Crutchfield and J.R. Van Wazer, Top. Phosphor. Chem., 5 (1967) 286, 446.
6 W. Lange, Ber., 61 (1928) 799; W. Lange and E. Müller, ibid., 63 (1930) 1058.
7 I.G. Ryss and V.B. Tul'chinskii, Zh. Neorg. Khim., 9 (1937) 836.
8 H.R. Clark and M.M. Jones, J. Amer. Chem. Soc., 92 (1970) 816.
9 H.R. Clark and M.M. Jones, Inorg. Chem., 10 (1971) 28.
10 J.E. Mahler and R. Pettit, J. Amer. Chem. Soc., 85 (1963) 3955.
11 G.W. Parshall and G. Wilkinson, Inorg. Chem., 1 (1962) 896.
12 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Second Edition, Wiley, New York, 1967, p. 633.
13 R.L. Bennett and M.I. Bruce, Aust. J. Chem., 28 (1975) 1141.
14 T.S. Sorensen and C.R. Jablonski, J. Organometal. Chem., 25 (1970) C62.