Applied Organometallic Chemistry (1987) 1 1–6

Cationic palladium(II) complexes of ferrocenylphosphines as homogeneous hydrogenation catalysts for olefins

William R Cullen and Nam Fong Han
Chemistry Department, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Received 20 November 1985 Accepted 28 April 1986

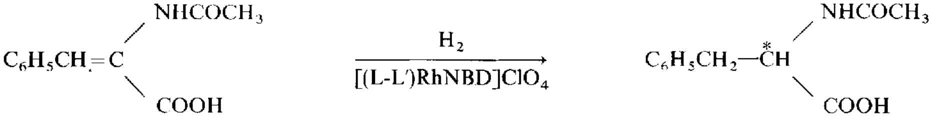
Cationic palladium(II) complexes of ferrocenylphosphines $[(L\text{-}L')Pd(S)_2][ClO_4]_2$ ((L-L′) = $Fe(\eta^5\text{-}C_5H_4P(C_6H_5)_2)_2$ 1, or $Fe(\eta^5\text{-}C_5H_5)(\eta^5$ $C_5H_3(CHMeNMe_2)P(C_6H_5)_2\text{-}1,2)$ 2a: S = pyridine or dimethylformamide) were prepared and characterized. The derivatives of 2a are effective catalysts for the hydrogenation of simple olefins at 30°C (1 atm H_2). The rate of reduction of styrene depends on the substrate concentration, catalyst concentration and the solvent, and is only slightly inhibited (16%) by the addition of mercury. These observations are consistent with a homogeneous catalytic system.

Keywords: Hydrogenation, reduction, catalyst, palladium, ferrocenylphosphanes, styrenes

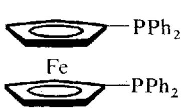
INTRODUCTION

Homogeneous hydrogenation catalysts comprising metal complexes of phosphines and arsines are well known[1–3] and many applications, particularly those concerned with asymmetric synthesis, utilize cationic rhodium(I) complexes such as $[(L\text{-}L')Rh(NBD)]ClO_4$. Here (L-L′) is a bidentate ligand, usually a di(tertiary phosphine) and optically active when necessary, and NBD is norbornadiene.[2,3] Such cationic complexes of **1** and **2** can be very effective catalysts and high optical yields are achieved in the reduction of amino acid precursors such as α-acylaminocinnamic acid, e.g. Eqn. 1 ((L-L′) = 2a).[4–10] Faster rates and increased optical yields can be achieved by changing the phosphine substituent ((L-L′) = 2b) or by using other ferrocenylphosphine ligands such as **2c** and **3**[8]. Thus, both steric and electronic effects of ligands seem to play a very important role in these catalyzed hydrogenation reactions and one of the advantages of using ligands based on the ferrocene skeleton is the ease with which both parameters can be varied.[4–10]

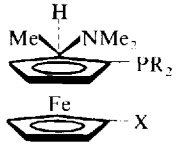
Only limited success has been achieved in attempts to use cationic derivatives of other Group 8 metals as hydrogenation catalysts. In particular Hartley and co-workers have reported[11–14] that both $[(dppe)PdCl(DMF)][ClO_4]$ in DMF, and $[(dppe)Pd(OCMe_2)_2][ClO_4]_2$ in



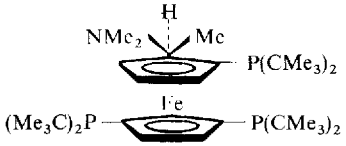
[1]



1



2a R = Ph, X = H
b R = CMe3, X = H
c R = Ph, X = PPh2



3

$CH_2Cl_2/OCMe_2$ (dppe = 1,2-bisdiphenylphosphinoethane) promoted the hydrogenation of styrene to ethylbenzene at 30°C and 1 atm. H_2. High catalyst to substrate ratios (1:5) were necessary to achieve reduction. The reactions were slow; in 72 h the conversion from the dication was quantitative but only 10% from the mono.

As part of our continuing studies on metal complexes of ferrocenylphosphines such as **1**–**3**, we now report that much more efficient hydrogenation catalysts can be prepared using the 'hard–soft' ligand **2a** in combination with palladium(II). Thus $[(L\text{-}L')PdS_2][ClO_4]_2$, L-L′ = **2a**, S = DMF, is almost as active a hydrogenation catalyst as the cationic rhodium(I) analogue as will be described below, and although simple palladium(II) complexes of **2a** such as $(L\text{-}L')PdCl_2$, have been used in catalyzed hydrosilylation and Grignard cross-coupling reactions,[17–19] this is the first report of their use as hydrogenation catalysts.

EXPERIMENTAL

Dichloromethane, nitromethane, pyridine and dimethylformamide were purified by literature methods.[20] Styrene, 1-hexene, cyclohexene were passed through an alumina column and freshly distilled before use. Silver perchlorate was dried at 60°C in vacuo. ^1H and $^{31}P\ \{^1H\}$ NMR spectra were recorded on Bruker WP-80 or Varian XL-100 spectrometers operating at 80 MHz (^1H) or 32.3 MHz or 40.5 MHz (^{31}P). ^{31}P chemical shifts are given relative to 85% H_3PO_4 with $P(OMe)_3$ ($\delta = +141.0$ ppm) used as an external reference. Reaction products were identified on the basis of their retention times on the carbowax column of a Hewlett Packard Model 5880A gas chromatograph. Infrared spectra were recorded on a Perkin–Elmer 590 spectrophotometer. Melting points were determined using a Gallenkamp melting point apparatus and are reported without correction. Microanalysis were performed by Mr P. Borda of the University of British Columbia. Hydrogenation reactions were carried out using a gas-uptake apparatus as described by James and Rempel.[21] The reaction conditions are given in Figs 1–4 and Tables 3 and 4.

The complexes $(L\text{-}L')PdCl_2$, (L-L′) = **1**, **2a** were prepared according to the literature procedures.[17–19] $[(L\text{-}L')Pd(S)_2][ClO_4]_2$, (L-L′) = **1**, **2a**; S = pyridine (pyr), dimethylformamide (DMF) were prepared essentially using the procedures of Hartley and co-workers,[11,12] but with some modifications as follows:

Preparation of $[(L\text{-}L')PdS_2][ClO_4]_2$; 4–7

All procedures were carried out in a Schlenk-type apparatus in a nitrogen atmosphere. The complex $(L\text{-}L')PdCl_2$ (0.5 mmol) was dissolved in a mixture of CH_2Cl_2 (20 cm^3) and the ligand S (10 cm^3); $AgClO_4$ (1 mmol) in CH_3NO_2 (10 cm^3) was added with stirring. After 3 h the precipitate was filtered off and the solution taken to dryness in vacuo. The residual oily solid was extracted with CH_2Cl_2 and the combined extracts were reduced to small volume in vacuo. Dropwise addition of anhydrous diethylether precipitated a solid product which was further purified by dissolving it in CH_2Cl_2 followed by reprecipitation with anhydrous diethylether. After filtration, the solid was dried in vacuo at room temperature. Analytical and spectroscopic data for the products are given in Tables 1 and 2.

Preparation of $[(L\text{-}L')PdCl(DMF)][ClO_4]$, 8

This was prepared in the same way as **5** except that 0.5 mmol of $AgClO_4$ was used.

RESULTS AND DISCUSSION

Cationic palladium(II) complexes of **1** and **2a**, **4**–**7**, were prepared as shown in Eqn. 2.

$$(L\text{-}L')PdCl_2 \xrightarrow[CH_2Cl_2/S]{AgClO_4} [(L\text{-}L')PdS_2][ClO_4]_2 + 2AgCl \qquad [2]$$

The analytical and spectroscopic data are in accord with their formulation. The IR spectra of all four complexes exhibit a broad band at 1090 cm^{-1} and a medium sharp band at 620 cm^{-1}; these are unsplit and indicate that the perchlorate ions do not interact with the cation.[22] The complexes **4** and **6** show bands at 1605 and 1220 cm^{-1} characteristic of coordinated pyridine.[23] Complexes **5** and **7** have a strong broad absorption at 1636 cm^{-1} consistent with carbonyl-oxygen coordinated DMF;[24] the ^1H NMR spectra support these conclusions.

The complex $[(L\text{-}L')PdCl(DMF)][ClO_4]$ (L-L′) = **1**, **8**, was prepared in a similar fashion and seems to have been isolated as the dihydrate. This complex is less stable than **4**–**7** and it is difficult to obtain reproducible results. This may be due to the partial formation of a chloride

Table 1 Analytical data for new complexes

Complex[a]	(L-L′)	S	m.p. (°C) (decomp)	Calcd. % C	H	N	Found % C	H	N
4	**1**	pyr	194–196	51.92	3.76	2.75	51.24	3.98	2.66
5	**1**	DMF	155–159	47.76	4.21	2.71	47.27	4.23	2.55
6	**2**a	pyr	158–163	47.78	4.23	4.64	47.35	4.34	5.00
7	**2**a	DMF	144–148	43.05	4.74	4.71	43.20	4.86	4.23
8[b]	**1**	Cl, DMF	145–148	49.13	4.31	1.55	49.77	4.22	1.79

[a] **4**, **6** are purple solids; **5**, **7**, **8**, are dark brown solids
[b] data are calculated for the dihydrate

Table 2 NMR spectroscopic data for new complexes[a]

Complex	^1H	$^{31}P(^1H)$
4	4.63, 4.80 (2 × bm, $Fe(C_5\underline{H}_4)_2$; 6.90–7.18, 7.20–7.45, 8.58–8.88 (3 × bm, $NC_5\underline{H})_5$; 7.48–8.03 (m, $P(C_6\underline{H}_5)_2$)	32.84(s)
5	3.08, 3.33 (2 × bs, $N(\underline{CH}_3)_2$; 4.65 (bs, $Fe(C_5\underline{H}_4)_2$: 7.38–8.15 (bm, $P(C_6\underline{H}_5)_2 + C\underline{H}O$)	43.23(s)
6	1.83 (bd, $CH\underline{CH}_3$); 2.50, 3.43 (2 × bs, $N(\underline{CH}_3))_2$); 3.90 (s, $Fe(C_5\underline{H}_5)$; 3.93–4.90 (m, $Fe(C_5\underline{H}_3) + \underline{CH}CH_3$; 6.75–7.08, 7.25–7.35, 8.15–8.73 (3 × bm, $NC_5\underline{H}_5$); 7.35–8.25 (m, $P(C_6\underline{H}_5)_2$).	20.20(s)[c]
7	1.65 (bd, $CH\underline{CH}_3$); 2.53, 3.80 (2 × bs, $N(\underline{CH}_3)_2$); 2.95, 3.30 (2 × bs, $CHON(\underline{CH}_3)_2$); 3.98 (s, $Fe(C_5\underline{H}_5)$); 4.3–4.88 (m, $Fe(C_5\underline{H}_3) + \underline{CH}CH_3$); 7.30–8.01 (m, $P(C_6\underline{H}_5)_2$); 8.31–8.63 (m, $C\underline{H}O$)[b].	19.20(s)[d]

[a] $CDCl_3$ was solvent unless otherwise stated
$^{31}P\{^1H\}$ for **1**, −17.76(s); **2**a, −22.02(s)
[b] CD_2Cl_2
[c] CH_2Cl_2
[d] DMF

bridged species as suggested by others for analogous derivatives of dppe.[11]

The five complexes **4**–**8** were examined with regard to their ability to catalyze the hydrogenation of styrene in DMF solution at 30°C and 1 atm H_2, and all except **4** were effective. The fastest rate was achieved with complex **7**, a derivative of the 'hard–soft' ligand **2**a. The lower reactivity of **4**, **5** and **8** which contain the di(tertiary phosphine) **1** is also consistent with the results of Hartley and co-workers, described in the Introduction for the ligand dppe, although, judging by the present results, the ferrocene skeleton does seem to have a positive effect on the rate of hydrogenation of styrene. Clark and co-workers[25] have made similar observations regarding the hydrogenation of styrene with the mixed monodentate platinum system $Pt(L)(L')Cl_2/SnCl_2 \cdot 2H_2O$, where the increase in catalytic activity with decreasing basicity of the weaker ligand L′ was taken as an indication that L′ functions as a leaving group. This effect is not noted in the $[(L\text{-}L')Rh(NBD)]^+$ catalyzed reduction; (L-L′) = **1** is a superior catalyst to **2**a.[16]

The nature of the ligand S is also important since for L-L′ = **1** the ease of reduction in the palladium system seems to be in the order $S_2 = (pyr)_2 < (Cl, DMF) < (DMF)_2$. The same order $(pyr)_2 < (DMF)_2$ is found for complexes of **2**a. Similar effects are probably responsible for the lower rates of hydrogenation found for derivatives of **2**a when the solvent is changed from

Table 3 Catalytic hydrogenation of olefins by complexes **4**–**8**[a]

Complex	Olefin	Solvent	Time (h)	Product	Chem. yield %[b]
4	styrene	DMF	24	no product	0
5	styrene	DMF	24	ethylbenzene	53
6	styrene	DMF	24	ethylbenzene	78
7	styrene	DMF	2.2	ethylbenzene	100
8	styrene	DMF	24	ethylbenzene	20
7	styrene	DMSO	2.2	ethylbenzene	56
7	styrene	pyr	2.2	ethylbenzene	22
7	l-hexene	DMF	2.2	n-hexane	61
7	cyclohexene	DMF	2.2	cyclohexane	40
7	α-arylaminocinnamicacid	DMF	24	no product	0
7	styrene	DMF[c]	2.2	ethylbenzene	24

[a] [Olefin] = 4.36×10^{-2} mol dm^{-3}; [Pd] = 8.72×10^{-4} mol dm^{-3} in 5 cm^3 of solvent used; 30°C, 1 atm total pressure of H_2

[b] GLC yield based on starting olefin

[c] In presence of excess **2a** (**2a**/[Pd] = 5/1)

DMF to the more strongly coordinating DMSO or pyridine.[26] When the reaction is carried out in DMF in the presence of excess ligand **2a** the rate is lowered as well suggesting competition for sites on the metal. Indeed the colour change in the reaction solution during the hydrogenation in the presence of excess **2a**, brown to orange, is not observed in its absence.

Addition of the base triethylamine to the reaction mixture results in enhancement of the rate of hydrogenating styrene, Table 4. This rate enhancement is diminished in the presence of a large excess of added base. A common interpretation of the rate enhancing effect of base on a reaction is that it encourages the heterolytic cleavage of hydrogen by the metal species by mopping up protons, however, it has recently been demonstrated that their role may be less innocent in that some amines can react with Group 8 derivatives forming M–C bonds.[27,28]

Table 4 Effect of Et_3N in hydrogenation of styrene by complex **7**[a]

Et_3N/Pd	Observed rate × 10^5, MS^{-1} [b]	Enhancement[c]
0:1	1.51	1.00
5:1	2.58	1.71
10:1	2.42	1.60
20:1	2.64	1.75
∞:1	2.08	1.38

[a] [Styrene] = 4.36×10^{-2} mol dm^{-3}; [**7**] = 8.72×10^{-4} mol dm^{-3} in 5 cm^3 DMF solution; 30°C. 1 atm total pressure of H_2, time 1 h

[b] Observed rate is the max. slope of the gas uptake plot

[c] Enhancement is the ratio of observed rate with Et_3N added to that with no Et_3N added

Complex **7** also catalyzes the hydrogenation of 1-hexene and cyclohexene in DMF solution. These reductions seem to be slower than styrene, a not unusual observation.[1c] A disappointing aspect of these results is seen in the failure of **7** to catalyze the hydrogenation of α-acylaminocinnamic acid which seems to eliminate possible use of these systems for asymmetric olefin hydrogenations. As noted in the Introduction, Eqn 1, [(L-L′)Rh(NBD)]ClO_4 (L-L′) = **2a** is a good catalyst for this reaction.[6,8] On the positive side, however, the hydrogenation of styrene catalyzed by **7** is faster than the same reaction catalyzed by the cationic rhodium(I) derivative.

Selected hydrogen uptake curves for the hydrogenation of styrene in DMF are shown in Fig. 1. After a small induction period smooth reduction takes place and is complete in a reasonable time when the substrate/catalyst ratio is 100/1. The maximum rate is lower when the ratio is decreased although the reaction is essentially complete in much the same time. Curve C shows the more sluggish uptake obtained in DMSO as solvent. The first order rate dependence of the reaction on the substrate, in DMF, is shown in Fig. 2. The rate dependence on catalyst is shown in Fig. 3. The data are limited but do seem to indicate an initial first order dependence which drops off with increase in concentration.

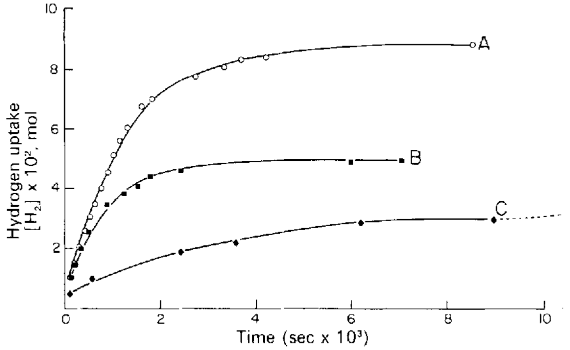


Figure 1 Hydrogen uptake curves for the hydrogenation of styrene catalyzed by complex **7** at 30°C and 1 atm total pressure. A, [styrene] = 8.72×10^{-2} mol dm^{-3}, [Pd] = 8.72×10^{-4} mol dm^{-3}, DMF (5 cm^3); B, [styrene] = 4.36×10^{-2} mol dm^3, [Pd] = 8.72×10^{-4} mol dm^{-3}, DMF (5 cm^3); C, [styrene] = 4.36×10^{-2} mol dm^{-3}, [Pd] = 8.72×10^{-4} mol dm^{-3}, DMSO (5 cm^3).

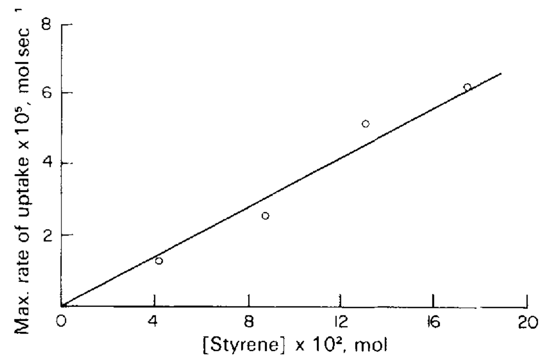


Figure 2 Dependence of maximum hydrogenation rate on [styrene]: DMF (5 cm^3) at 30°C, 1 atm total pressure; [Pd] = 8.72×10^{-4} mol dm^{-3}.

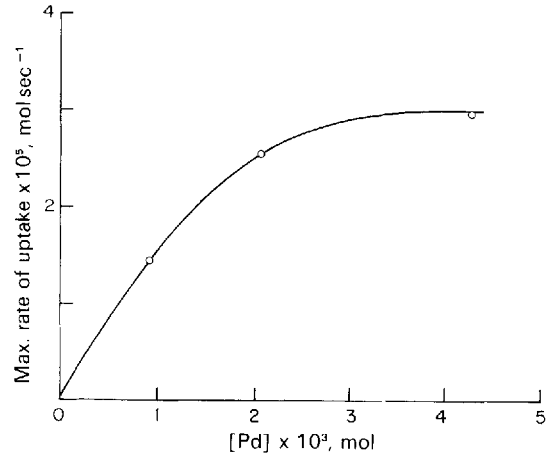


Figure 3 Dependence of maximum hydrogenation rate on [Pd]: DMF (5 cm^3) at 30°C, 1 atm total pressure, [styrene] = 4.36×10^{-2} mol dm^{-3}.

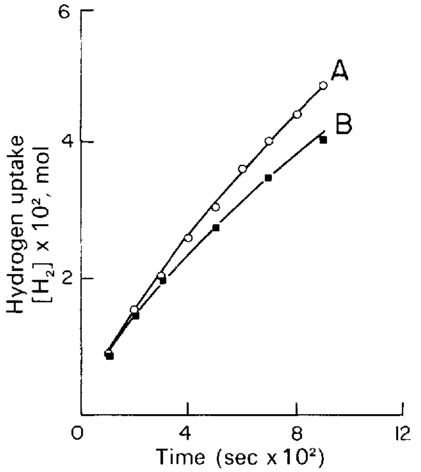


Figure 4 Hydrogen uptake curves for the hydrogenation of styrene (first 15 minutes). A, same condition as A in Figure 1. B, same condition as A with Hg added.

These results are consistent with a homogeneous system but to confirm this conclusion the reduction was performed in the presence of excess mercury.[29] The data are shown in Fig. 4. Some inhibition by mercury does occur (~16%) by comparison of maximum rate values; however the effect would be expected to be much greater if the system were heterogeneous.[29]

Many mechanisms are possible for this reaction although a hydride route involving initial oxidative addition seems unlikely. In the absence of substrate the catalyst **7** absorbs slightly more than 2 moles of H_2 per mole of Pd which suggests metal hydride formation but no hard evidence is yet available for this or to account for the observed rate dependences and the superiority of the 'hard–soft' ligand **2a** which could conceivably be acting as a 'hinge' on the metal by the dissociation of the $-NMe_2$ group.[5,7]

CONCLUSION

In conclusion the most significant finding of the present work is that cationic homogeneous hydrogenation catalysts based on the relatively inexpensive metal, palladium, can be prepared. Although, these reduce a narrower range of substrates than their cationic rhodium(I) counterparts this may be a benefit in allowing greater selectivity.

Acknowledgements We thank the Natural Sciences and Engineering Research Council of Canada for financial support, Dr F. R. Hartley for valuable discussion, Dr T. G. Appleton for some ^{31}P NMR data, and Johnson Matthey Limited for the loan of palladium salts.

REFERENCES

1. Marko, L and Bakos J In: *Aspects of homogeneous catalysis*, Vgo, R (ed), Reidel Publishing Co., Dordrecht, 1981, Vol. 4, p 145
   (b) *Homogeneous catalysis with metal phosphine complexes*, Pignolet, LM (ed), Plenum Press, New York, 1983
   (c) James, BR *Homogeneous hydrogenation*, Wiley, New York, 1973
   (d) James, BR In: *Comprehensive Organometallic Chemistry*, Wilkinson, G, Stone, FGA and Abel, EW (eds) Pergamon Press, Oxford, 1982, Vol. 8, p 33
2. Halpern, J *Science*, 1982, 217: 401
3. Kagan, H In: *Comprehensive Organometallic Chemistry*, Wilkinson, G, Stone, FGA and Abel, EW (eds) Pergamon Press, Oxford, 1982, Vol. 8, p 463
4. Cullen, WR and Woollins, JD *Coord. Chem. Rev.*, 1982, 39: 1
5. Hayashi, T and Kumada, M *Acc. Chem. Res.*, 1982, 15: 395
6. Cullen, WR, Einstein, FWB, Willis, AC and Yeh, ES *J. Am. Chem. Soc.*, 1980, 102: 988
7. Cullen, WR and Woollins, JD *Can. J. Chem.* 1982, 60: 1793
8. Appleton, TD, Cullen, WR, Evans, SV, Kim, TJ and Trotter, J *J. Organomet. Chem.* 1985, 279: 5
9. Butler, IR, Cullen, WR and Kim, TJ *Synth. React. Inorg. Metal-Org. Chem.*, 1985, 15: 109
10. Hayashi, T, Mise, T, Fukushima, M, Kogotani, M, Nagashima, N, Hamada, Y, Matsumoto, A, Kawakami, S, Konishi, M, Yamamoto, K and Kumada, M *J. Chem. Soc. Jpn.* 1980, 53: 1138
11. Davies, JA, Hartley, FR and Murray, SG *Inorg. Chem.*, 1980, 19: 2299
12. Davies, JA, Hartley, FR and Murray, SG *J. Chem. Soc. Dalton Trans.*, 1980, 2246
13. Davies, JA, Hartley, FR, Murray, SG and Marshall, G *J. Mol. Catal.*, 1981, 10: 171
14. Davies, JA and Hartley, FR *Reviews in Inorg. Chem.*, 1982, 4: 27
15. Butler, IR, and Cullen, WR, *Can. J. Chem.*, 1983, 61: 2354
16. Cullen, WR, Kim, TJ, Einstein, FWB and Jones, T *Organometallics*, 1983, 2: 714
17. Hayashi, T, Tamao, K, Katsuro, Y, Nakae, I and Kumada, M *Tetrahedron Lett.*, 1980, 21: 1871
18. Hayashi, T, Konishi, M, Fukushima, M, Mise, T, Kagotang, M, Tafika, M and Kumada, M *J. Am. Chem. Soc.*, 1982, 104: 180
19. Hayashi, T, Konishi, M, Kobori, Y, Kumada, M, Higuchi, T and Hirotsu, K *J. Am. Chem. Soc.*, 1984, 106: 158
20. Vogel, AI *Textbook of Practical Organic Chemistry*, 4th Ed., Longman, London, 1978
21. James, BR and Rempel, G *Can. J. Chem.*, 1966, 44: 233
22. Pavkovic, SF and Meek, DW *Inorg. Chem.*, 1965, 4: 1091
23. Gill, NS, Nuttall, RH, Scaife, DE and Sharp, DWA *J. Inorg. Nucl. Chem.*, 1961, 18: 79
24. Wayland, BB and Schramm, RF *Inorg. Chem.* 1969, 8: 971
25. Clark, HC, Billard, C and Wong, CS *J. Organomet. Chem.*, 1980, 190: C105
26. Drago, RS and Purcell, KF *Non-aqueous solvent systems*, Waddington, TC (ed), Academic Press, London, 1965, p 212
27. (a) Laine, RM, Thomas, DW, Cary, LW and Buttrill, SE *J. Am. Chem. Soc.*, 1978, 100: 6527
   (b) Gamage, S. Morris, RH, Rettig, SJ and James, BR *J. Organomet. Chem.*, in press
28. McRindle, R, Ferguson, G, Arsenault, GJ and McAlees, AJ *J. Chem. Soc., Chem. Commun.*, 1983, 571
29. Crabtree, RH and Anton, DR *Organometallics*, 1983, 2: 855