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Journal of Organometallic Chemistry 637–639 (2001) 767–771

Journal of Organometallic Chemistry

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Note

Reactivity of the bis(allyl)-ruthenium(IV) dimer $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ $(C_{10}H_{16} = 2,7\text{-dimethylocta-2,6-diene-1,8-diyl})$ towards dppf $(\text{dppf} = [Fe(\eta^5\text{-}C_5H_4PPh_2)_2])$ and dppfO $(\text{dppfO} = [Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4P(=O)Ph_2)])$

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Received 2 January 2001; received in revised form 22 February 2001; accepted 22 February 2001

Abstract

The bis(allyl)-ruthenium(IV) derivative $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ reacts with dppf and dppfO to yield complexes $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-dppf})]$ and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-dppfO})]$, respectively. The electrochemical data of these complexes are reported. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 1,1′-Bis(diphenylphosphino)ferrocene; $\eta^3{:}\eta^3$-Octadienediyl complexes; Bis(allyl) complexes; Ruthenium(IV) complexes

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1. Introduction

Bis(allyl)-ruthenium(II) derivatives $[Ru(\eta^3\text{-}2\text{-}RC_3H_4)_2L_2]$ (R = H, Me; L_2 = chiral or achiral diphosphine) have attracted a great deal of attention in recent years due to their useful applications in catalytic organic synthesis [1]. In contrast, much less attention has been devoted to the preparation of mononuclear bis(allyl)-ruthenium(IV) complexes containing chelating diphosphines [2]. This is rather surprising given that $\eta^3{:}\eta^3$-octadienediyl-ruthenium(IV) derivatives such as the chloro-bridged dimer $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) [3] or the mononuclear complex $[Ru(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})Cl_2]$ ($C_{12}H_{18}$ = dodeca-2,6,10-triene-1,12-diyl) [4], known since the 1960s, are readily available from the reaction of ethanolic ruthenium trichloride and isoprene or butadiene, respectively. Moreover, the unusual properties exhibited by the dimeric complex $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (**1**) and some of its derivatives, namely, remarkable stability, water solubility [5], and catalytic activity in ROMP of cycloolefins [5b,6] and butadiene polymerization [7], make **1** a source of considerable interest. Although the molecular structure of **1** in the solid state shows an overall C_i symmetry (see Fig. 1) [3b], in solution it exists as an approximately equimolar mixture of two diastereoisomers, referred to as the C_i (*meso*) and C_2 (*rac*) forms (Fig. 1), arising as a conse-

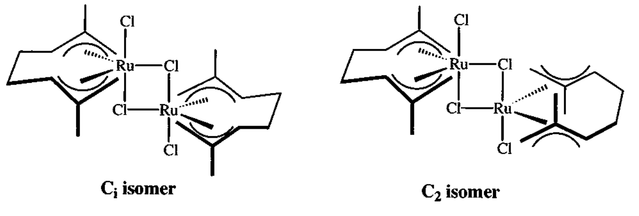

Fig. 1. The two diastereomeric forms of $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (**1**).

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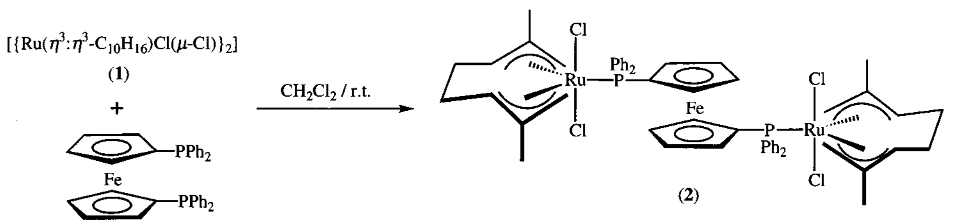
PII: S0022-328X(01)00914-7



Scheme 1.

quence of the three ways of joining together the two chiral (η^3:η^3-$C_{10}H_{16}$)Ru units [8].

Dimer **1** shows a versatile chemistry with preservation of the bis(allyl) unit. Thus, chloride bridging cleavage using neutral and anionic ligands is the starting point for the preparation of wide series of: (a) mononuclear [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2L] (L = phosphines, phosphites, CO, nitriles, amines, thiols, etc.) [8,9] and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-L–L)] (L–L = dithiocarbamates, semicarbazides, acetates, pyridine-2-thiolate, nitrate, etc.) [5a,10] derivatives, and (b) dinuclear ligand-bridged [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-L–L)] (L–L = diamines, dppm) [9d,11] and [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-L)}$_2$] (L = thiolates, thiocyanate, selenocyanate, etc.) [9e,12] complexes. In addition, cationic species [Ru(η^3:η^3-$C_{10}H_{16}$)ClL$_2$]$^+$ (L = isocyanides, trimethylphosphite, acetone, acetonitrile; L$_2$ = chelating diamines) and [Ru(η^3:η^3-$C_{10}H_{16}$)L$_3$]$^{2+}$ (L = acetone, acetonitrile, L$_3$ = 2,2′:6,2″-terpyridine) have been also prepared by treatment of **1** with the appropriate two-electron ligands in the presence of $AgBF_4$ [6d,9c, 9d,10f,11b].

With all these precedents in mind we wondered about the possibility of using the dimeric complex **1** as a suitable starting material for the preparation of bis(allyl)-ruthenium(IV) complexes containing chelating diphosphines. Thus, we present herein our studies on the reactivity of **1** towards the versatile diphosphine ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) and its monoxide dppfO [13].

2. Results and discussion

The dimeric bis(allyl)-ruthenium(IV) complex [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (**1**) reacts with one equivalent of dppf [14], in dichloromethane at room temperature, to afford the trinuclear derivative [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppf)] (**2**; 91% yield) (Scheme 1).

Compound **2** is an air-stable solid soluble in polar solvents (e.g. dichloromethane or acetone). It has been characterized by elemental analyses and IR and NMR (^{31}P{^{1}H}, ^{1}H and ^{13}C{^{1}H}) spectroscopy (for details see Section 4) being its dimeric nature confirmed clearly by the relative intensities of the octadienediyl and diphosphine resonances (2:1) in the ^{1}H-NMR spectrum. Significantly, the ^{31}P{^{1}H}-NMR spectrum displays two singlet signals in ca. 1:1 ratio (18.31 and 18.55 ppm). This fact seems to indicate the presence of two different isomers in solution. Although we have not carried out detailed variable-temperature NMR experiments, we note that when a solution of **2** in CD_2Cl_2 is cooled below 293 K the ^{31}P{^{1}H}-NMR spectra show only one broad signal indicating that an interconversion process between conformational isomers is taken place. The presence of an equimolar mixture of two energetically favoured conformational isomers with overall C_i symmetry (confirmed by X-ray diffraction analysis) has been reported previously for the related dinuclear complex [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppm)] (dppm = bis(diphenylphosphino)methane) [11a]. ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **2** display only one set of resonances for the η^3:η^3-$C_{10}H_{16}$ moiety with their two halves in apparent equivalent environments (i.e. only five resonances are observed in the ^{13}C{^{1}H}-NMR spectrum). This is rather surprising since a doubling of signals should be expected as a consequence of the presence of two different isomers in solution [11a].

It is noteworthy that compound **2** is also obtained by treatment of **1** with an excess of dppf. This result contrasts with that shown by the diphosphine ligand dppm for which the mononuclear adduct [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-dppm)] is isolated [11a]. The different behaviour observed for dppm and dppf is most likely due to the steric requirements of the bulky η^3:η^3-octadienediyl-Ru(IV) fragment. It seems that the steric hindrance between the two [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2] units, which increases when the bridged diphosphine dppf is replaced by the smaller dppm ligand, leads to the isolation of the mononuclear derivative [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-dppm)]. All attempts to prepare the cationic species [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P*,*P*-dppf)]-[BF_4] by treatment of dimer **1** with two equivalents of dppf and $AgBF_4$ in dichloromethane, acetone or acetonitrile have been unsuccessful obtaining instead mixtures of uncharacterized products. Apparently, the tendency of dppf to act as a bridging ligand in **2** also prevents the formation of the desired chelated complex.

Taking into account the lower ability of diphosphine-monoxides to act as bridging ligands [15], we became interested in studying the reactivity of dimer **1** towards dppfO [16] in order to prepare the chelated derivative

$[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl(\kappa^2-P,O-dppfO)]^+$. Thus, we have found that complex **1** reacts with a twofold excess of dppfO to generate the neutral dinuclear adduct $[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2(\kappa^1-P-dppfO)]$ (**3**; 67% yield) as the result of the selective coordination of the diphenylphosphino group on the Ru(IV) center (Scheme 2). As expected, no dinuclear bridged products were detected even when the reaction was carried out with only one equivalent of dppfO obtaining instead an equimolar mixture of **3** and the precursor complex **1**.

Characterization of **3** was achieved unequivocally by means of spectroscopic techniques (IR and $^{31}P\{^1H\}$-, ^1H- and $^{13}C\{^1H\}$-NMR) as well as elemental analyses (see Section 4). Remarkably, while the ^1H spectrum displays a single set of signals for the two allylic moieties of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand, as expected for the formation of simple equatorial adduct $[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2L]$ [8,9], the $^{13}C\{^1H\}$-NMR spectrum shows two different resonances for the C_1/C_8 (69.03 (d, $J_{CP} = 4.9$ Hz) and 70.26 (s) ppm) and C_3/C_6 (107.50 (d, $J_{CP} = 6.6$ Hz) and 107.71 (d, $J_{CP} = 6.6$ Hz) ppm) atoms of the octadienediyl skeleton (for numbering see Section 4) suggesting that the two halves of the ligand are in inequivalent environments. This inequivalence, which should be also observed for the trinuclear complex **2**, can be explained assuming that the molecule is locked in a given conformation due to a restricted rotation about the Ru–P bond which could arise from the steric requirements of the octadienediyl and ferrocenyl bulky groups. Significantly, all attempts to form the cationic derivative $[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl(\kappa^2-P,O-dppfO)][BF_4]$ by treatment of **3** with $AgBF_4$ or starting directly from **1** have been unsuccessful obtaining instead mixtures of uncharacterized products. Once again, this behaviour can be attributed to the steric hindrance between the metallic fragment and the bulky ferrocenyl ligand which prevents its chelation.

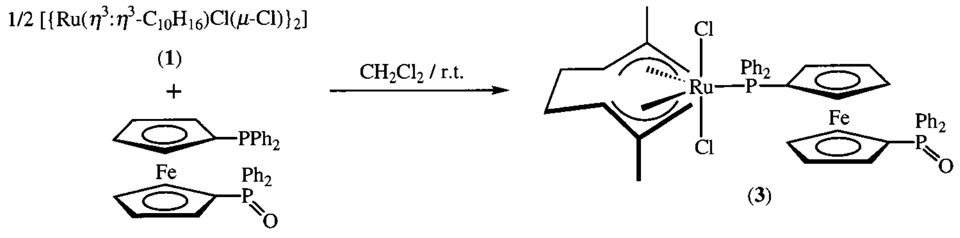
Complexes incorporating ferrocenyl units are expected to exhibit a ferrocene-centered oxidative process. The redox behaviour of free dppf has been studied by several groups [17], being accepted that undergoes an initial ferrocene-based reversible oxidation followed by a fast chemical reaction involving the phosphorus substituents on the cyclopentadienyl rings [17e]. Electrochemical studies on transition-metal complexes containing coordinated dppf normally show irreversible ferrocene-based oxidations due to the high lability of the oxidized ligand [13,17]. In contrast, cyclic voltammetry (CV) studies on dichloromethane solutions of $[\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2\}_2(\mu-dppf)]$ (**2**) and $[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2(\kappa^1-P-dppfO)]$ (**3**) show that these complexes undergo one-electron oxidation ($E^{\circ\prime} = 0.27$ (**2**) and 0.38 (**3**) V), which is chemically reversible under the experimental conditions (scan rate: 100 mV s^{-1}). Reversible oxidations of coordinated dppf are also known for the complexes $[MCl_2(dppf)]$ (M = Pd, Pt) [17b].

3. Conclusions

It is well-known that the bidentate ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) shows a versatile coordination chemistry adapting its bite angle to the geometric requirements of the metal fragment through the appropriate ring twisting or tilting [13]. Although the chelating coordination mode is the predominant character of dppf in most metal centers to which it is attached, a large number of homo- and heteropolinuclear complexes containing bridging dppf are known. In this paper, a clear example of the ability of dppf to act as a bridging ligand, i.e. $[\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2\}_2(\mu-dppf)]$, has been presented and rationalized as the result of the steric hindrance between the bulky ferrocenyl and bis(allyl)-ruthenium(IV) fragments. Steric requirements seem also to be responsible of the non chelation of dppfO from the neutral adduct $[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2(\kappa^1-P-dppfO)]$. These results contrast with those observed using bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane and their diphosphine-monoxide counterparts which are able to coordinate in a chelating fashion on the sterically demanding $Ru(\eta^3:\eta^3-C_{10}H_{16})$ moiety [18].

4. Experimental

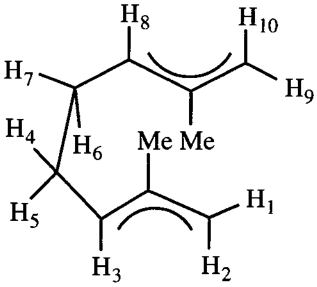
The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. Com-

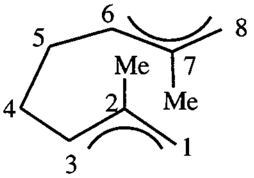


Scheme 2.

pounds $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (**1**) [10a], dppf [14] and dppfO [16] were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The C and H analyses were carried out with a Perkin–Elmer 240-B microanalyzer. Cyclic voltammetry (CV) measurements (25 °C) were carried out with a three-electrode system. The working electrode was a platinum disk electrode, the counter electrode was a platinum spiral, and the reference electrode was an aqueous saturated calomel electrode (SCE) separated from the solution by a porous septum. Current and voltage parameters were controlled using a PAR system M273. In a typical experiment, 1.5×10^{-2} mmol of the complex was dissolved under a nitrogen atmosphere in 10 ml of freshly distilled and deoxygenated dichloromethane containing 1.15 g of pure $[NBu_4][PF_6]$ (0.3 mmol) as electrolyte. Formal CV potentials ($E^{\circ\prime}$) are referenced relative to potential of the $[Cp_2Fe]/[Cp_2Fe]^+$ couple ($E^\circ = 0.22$ V) run under identical conditions ($E^{\circ\prime} = E^\circ(\text{Complex}^+/\text{Complex}) - E^\circ([Cp_2Fe]^+/[Cp_2Fe])$) [19]. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported.

The numbering for protons and carbons of the octadienediyl skeleton are as follows:





4.1. Synthesis of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-dppf})]$ (2)

A solution of 0.300 g (0.487 mmol) of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**) in 30 ml of dichloromethane was treated at room temperature (r.t.) with 0.270 g (0.487 mmol) of dppf. After stirring for 5 min, the solvent was removed under vacuum and the resulting orange solid residue washed with hexanes (3 × 20 ml) and dried in vacuo. Yield: 0.518 g (91%). Anal. Calc. for $FeRu_2C_{54}H_{60}Cl_4P_2$ (1170.82): C, 55.39; H, 5.16. Found: C, 54.67; H, 4.98%; IR (KBr, cm^{-1}): 1431 (s), 1155 (s), 1089 (s), 1040 (s), 1021 (s), 746 (s), 693 (vs), 512 (s), 470 (s); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ 18.31 (s), 18.55 (s) ppm; ^{1}H-NMR ($CDCl_3$) δ 2.07 (s, 12H, CH_3), 2.54 (m, 4H, H_4 and H_6), 2.93 (m, 4H, H_2 and H_{10}), 3.33 (m, 4H, H_5 and H_7), 3.83 (m, 4H, H_1 and H_9), 3.86–3.90 (m, 6H CH of C_5H_4), 4.26 and 4.35 (br, 1H each one, CH of C_5H_4), 5.07 (m, 4H, H_3 and H_8), 7.30–7.90 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ 20.85 (s, CH_3), 36.77 (s, C_4 and C_5), 69.15 (s, C_1 and C_8), 72.60, 72.63, 73.00 and 73.05 (d, $J_{CP} = 7.6$ Hz, CH of C_5H_4), 75.62, 76.06, 76.44 and 76.81 (d, $J_{CP} = 9.5$ Hz, CH of C_5H_4), 83.08 and 83.13 (d, $J_{CP} = 41.4$ Hz, C of C_5H_4), 107.54 (d, $J_{CP} = 10.2$ Hz, C_3 and C_6), 125.82 (s, C_2 and C_7), 127.00–136.00 (m, Ph) ppm.

4.2. Synthesis of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-dppfO})]$ (3)

A solution of 1.078 g (1.75 mmol) of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**) in 20 ml of dichloromethane was treated at r.t. with 1.996 g (3.5 mmol) of dppfO. After stirring for 5 min, the solvent was removed under vacuum and the resulting orange solid residue washed with diethyl ether (3 × 20 ml) and dried in vacuo. Yield: 2.06 g (67%). Anal. Calc. for $FeRuC_{44}H_{44}Cl_2P_2O$ (878.61): C, 60.15; H, 5.04. Found: C, 59.75; H, 5.17%; IR (KBr, cm^{-1}): 1435 (s), 1261 (vs), 1209 (s), 1169 (s), 1098 (vs), 1024 (vs), 800 (vs), 697 (s), 567 (s); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ 18.73 (s, Ph_2P), 28.97 (s, $Ph_2P{=}O$) ppm; ^{1}H-NMR ($CDCl_3$) δ 2.09 (s, 6H, CH_3), 2.54 (m, 2H, H_4 and H_6), 2.97 (d, 2H, $J_{HP} = 3.7$ Hz, H_2 and H_{10}), 3.34 (m, 2H, H_5 and H_7), 3.98 (d, 2H, $J_{HP} = 9.1$ Hz, H_1 and H_9), 3.88–4.62 (m, 8H, CH of C_5H_4), 5.07 (m, 2H, H_3 and H_8), 7.35–7.90 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ 20.88 (s, CH_3), 36.81 (s, C_4 and C_5), 69.03 (d, $J_{CP} = 4.9$ Hz, C_1 or C_8), 70.26 (s, C_1 or C_8), 71.89 and 72.10 (d, $J_{CP} = 7.8$ Hz, CH of C_5H_4), 73.46 and 73.81 (d, $J_{CP} = 12.4$ Hz, CH of C_5H_4), 74.38 (d, $J_{CP} = 114.6$ Hz, C of C_5H_4), 74.75 and 75.01 (d, $J_{CP} = 10.3$ Hz, CH of C_5H_4), 75.75 and 77.19 (d, $J_{CP} = 9.2$ Hz, CH of C_5H_4), 83.09 (d, $J_{CP} = 41.6$ Hz, C of C_5H_4), 107.50 and 107.71 (d, $J_{CP} = 6.6$ Hz, C_3 and C_6), 125.75 (d, $J_{CP} = 1.2$ Hz, C_2 and C_7), 127.00–137.00 (m, Ph) ppm.

Acknowledgements

This work was supported by the Dirección General de Investigación Científica y Técnica of Spain (DGICYT, project PB96-0558).

References

[1] See for example:
(a) J.P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, S. Mallart, X. Pfister, L. Bischoff, M.C. Caño De Andrade, S. Darses, C. Galopin, J.A. Laffitte, Tetrahedron: Asymmetry 5 (1994) 675 and references cited therein;
(b) W. Leitner, C. Six, Chem. Ber./Recueil 130 (1997) 555;
(c) C. Bruneau, P.H. Dixneuf, Chem. Commun. (1997) 507 and references cited therein;

(d) V. Ratovelomanana-Vidal, J.P. Genêt, J. Organomet. Chem. 567 (1998) 163 and references cited therein;
(e) C. Six, B. Gabor, H. Görls, R. Mynott, P. Philipps, W. Leitner, Organometallics 18 (1999) 3316;
(f) C. Six, K. Beck, A. Wegner, W. Leitner, Organometallics 19 (2000) 4639.

[2] H. Werner, G. Fries, B. Weberndörfer, J. Organomet. Chem. 607 (2000) 182.

[3] (a) L. Porri, M.C. Gallazzi, A. Colombo, G. Allegra, Tetrahedron Lett. 47 (1965) 4187;
(b) A. Colombo, G. Allegra, Acta Crystallogr. Sect. B 27 (1971) 1653.

[4] (a) J.E. Lydon, J.K. Nicholson, B.L. Shaw, M.R. Truter, Proc. Chem. Soc. (1964) 421;
(b) J.K. Nicholson, B.L. Shaw, J. Chem. Soc. A (1966) 807;
(c) J.E. Lydon, M.R. Truter, J. Chem. Soc. A (1968) 362.

[5] (a) S.O. Sommerer, G.J. Palenik, Organometallics 10 (1991) 1223;
(b) S. Wache, J. Organomet. Chem. 491 (1995) 235.

[6] (a) K. Hiraki, A. Kuroiwa, H. Hirai, J. Polym. Sci. Sect. A1 9 (1971) 2323;
(b) L. Porri, R. Rossi, P. Diversi, A. Lucherini, Macromol. Chem. 175 (1974) 3097;
(c) S. Wache, W.A. Herrmann, G. Artus, O. Nuyken, D. Wolf, J. Organomet. Chem. 491 (1995) 181;
(d) W.A. Herrmann, W.C. Schattenmann, O. Nuyken, S.C. Glander, Angew. Chem. Int. Ed. Engl. 35 (1996) 1087.

[7] K. Hiraki, H. Hirai, Macromolecules 3 (1970) 382.

[8] D.N. Cox, R. Roulet, Inorg. Chem. 29 (1990) 1360.

[9] (a) R.A. Head, J.F. Nixon, J.R. Swain, C.M. Woodard, J. Organomet. Chem. 76 (1974) 393;
(b) P.B. Hitchcock, J.F. Nixon, J. Sinclair, J. Organomet. Chem. 86 (1975) C34;
(c) D.N. Cox, R.W.H. Small, R. Roulet, J. Chem. Soc. Dalton Trans. (1991) 2013;
(d) J.W. Steed, D.A. Tocher, J. Organomet. Chem. 471 (1994) 221;
(e) G. Belchem, J.W. Steed, D.A. Tocher, J. Chem. Soc. Dalton Trans. (1994) 1949;
(f) A.N. Sahay, D.S. Pandey, M.G. Walawalkar, J. Organomet. Chem. 613 (2000) 250.

[10] (a) J.G. Toerien, P.H. van Rooyen, J. Chem. Soc. Dalton Trans. (1991) 1563;
(b) J.W. Steed, D.A. Tocher, Inorg. Chim. Acta 189 (1991) 135;
(c) J.W. Steed, D.A. Tocher, J. Chem. Soc. Dalton Trans. (1992) 2765;
(d) B. Kavanagh, J.W. Steed, D.A. Tocher, J. Chem. Soc. Dalton Trans. (1993) 327;
(e) J.W. Steed, D.A. Tocher, Polyhedron 13 (1994) 167;
(f) G. Belchem, D.H.A. Schreiber, J.W. Steed, D.A. Tocher, Inorg. Chim. Acta 218 (1994) 81.

[11] (a) J.G. Toerien, P.H. van Rooyen, J. Chem. Soc. Dalton Trans. (1991) 2693;
(b) J.W. Steed, D.A. Tocher, Polyhedron 11 (1992) 2729.

[12] (a) J.W. Steed, D.A. Tocher, J. Chem. Soc. Dalton Trans. (1992) 459;
(b) J.W. Steed, D.A. Tocher, Polyhedron 11 (1992) 1849;
(c) M. Rowley, J.W. Steed, D.A. Tocher, Polyhedron 14 (1995) 1415.

[13] For a review on the chemistry of dppf and dppfO see: F.S. Gan, T.S.A. Hor, in: A. Togni, T. Hayashi (Eds.), Ferrocenes: Homogeneous Catalysis, Organic Synthesis and Materials Science, Ch. 1, VCH, Weinheim, 1995, p. 3.

[14] (a) G. Marr, T. Hunt, J. Chem. Soc. C (1969) 1070;
(b) J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichetenberg, R.E. Merrill, J.C. Smart, J. Organomet. Chem. 27 (1971) 241.

[15] For a review on the chemistry of hemilabile P/O-donor ligands see: A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.

[16] V.V. Grushim, J. Am. Chem. Soc. 121 (1999) 5831.

[17] (a) D.L. DuBois, C.W. Eigenbrot, A. Miedaner, J.C. Smart, R.C. Haltiwanger, Organometallics 5 (1986) 1405;
(b) B. Corain, B. Longato, G. Favero, D. Ajó, G. Pilloni, U. Russo, F.R. Kreissl, Inorg. Chim. Acta 157 (1989) 259;
(c) T.M. Miller, K.J. Ahmed, M.S. Wrighton, Inorg. Chem. 28 (1989) 2347;
(d) C.E. Housecroft, S.M. Owen, P.R. Raithby, B.A.M. Shaykh, Organometallics 9 (1990) 1617;
(e) G. Pilloni, B. Longato, B. Corain, J. Organomet. Chem. 420 (1991) 57.

[18] V. Cadierno, S.E. García-Garrido, J. Gimeno, unpublished results.

[19] (a) G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461;
(b) N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.