ELSEVIER

Journal of Organometallic Chemistry 625 (2001) 236–244

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Lithiation studies of $[PhP(CH_2Ph)_3]Cl$; X-ray crystal structure of the phosphoniodiylide $[(TMEDA)Li(PhCH)_2PPh(CH_2Ph)]$ and its rhodium and chromium complexes

Philip J. Bailey *, Tony Barrett, Simon Parsons

Department of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK

Received 7 November 2000; received in revised form 3 January 2001; accepted 3 January 2001

Abstract

Treatment of the phosphonium salt $[PhP(CH_2Ph)_3]Cl$ with three molar equivalents of ^nBuLi gives the dilithiated species $[Li_2PhP(CHPh)_3]$. The crystal structure of the monolithiated species as its TMEDA adduct has been determined. Treatment of the dilithiate species with $[((\eta\text{-}C_5Me_5)MX_2]_2$ (M = Cr, X = Br; M = Rh, X = Cl) provides $[(\eta\text{-}C_5Me_5)M\{\eta^2\text{-}PhP(CH_2Ph)(CHPh)_2\}X]$ containing chelating phosphoniodiylide ligands which are thought to be the hydrolysis products of the target complexes $[\{PhP(CHPh)_3\}M(C_5Me_5)]$.

Keywords: Lithiation; X-ray crystal structures; Phosphoniodiylide; Pentamethylcyclopentadienyl

1. Introduction

A large number of complexes containing the trimethylenemethane (TMM) ligand $[C(CH_2)_3]$ have now been characterised [1–3]. Until quite recently they were almost exclusively restricted to those of the middle and late transition metals, research in this area being fuelled partly by the application of Pd-TMM complex intermediates in [3 + 2] cycloaddition reactions [4]. However, an increasing number of high oxidation state early transition metal examples are now being reported [2,3], and the ligands appear well suited for coordination to these more electropositive centres. Potential applications of TMM as a dianionic replacement for cyclopentadienyl in α-alkene polymerisation applications has recently been discussed and investigated [3].

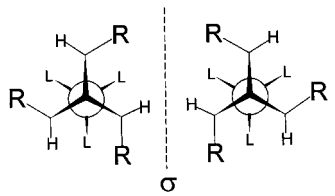

Fig. 1. C_3 symmetric arrangement of groups around trisubstituted trimethylenemethane and related ligands.

We realised some time ago that complexes containing ligands of the TMM type with a single substituent on each arm of the ligand framework could adopt chiral conformations with C_3 symmetry [5], and thus belong to a small class of ligands which occupy three fac coordination sites, and provide three equivalent chiral (homotopic) environments for substrate coordination opposite the ligand, in an octahedral complex (Fig. 1) [6]. The potential for application of such complexes in enantioselective catalytic processes, which involve octahedral intermediates is clear and has been the subject of a recent review article [7]. Such ligands are complementary to the well-established chiral C_2 symmetric ligands, most commonly diphosphines, which serve a similar purpose in square planar geometry [8].

Although trimethylenemethane complexes are readily available by a number of routes, the synthetic difficulties involved in the preparation of complexes of trisubstituted derivatives $[C(CHR)_3]$ mean that this class of ligand is unlikely to be widely applicable and we have therefore sought alternative ligand systems with the same symmetry properties. Our initial approach was to exploit the generally more facile synthe-

* Corresponding author.
E-mail address: philip.bailey@ed.ac.uk (P.J. Bailey).

0022-328X/01/$ - see front matter
PII: S0022-328X(01)00674-X

ses of nitrogen based systems in an investigation of the nitrogen analogues of TMM, $[C(NR)_3]^{2-}$ [5]. However, although these proved to be interesting chelating and bridging ligands [9,10], the distortion from planarity required for the η^3-coordination of such Y-shaped ligands is thought to be precluded by the energy associated with the in-plane π-bonding in such systems. This energy is increased in comparison to that for the $[C(CH_2)_3]^{2-}$ system by the replacement of the methylene carbon atoms by the more electronegative nitrogen. In order to address this problem we have begun an investigation of ligands in which the required distortion is built-in to the ligand before coordination, and to this end we are employing ligands centred on tetrahedral rather than trigonal planar atoms. We have previously reported initial studies on the potentially tridentate nitrogen donor system $[RP(NR)_3]^{2-}$ which was found to be a very powerful π-donating, chelating ligand, but were unable to demonstrate the coordination of the third nitrogen [11]. Here we report of investigations of the carbon-donor system $[RP(CHR)_3]^{2-}$ which is incapable of π-donation in this fashion. Mono- and dilithiation of the phosphonium salt $[PhP(CH_2Ph)_3]Cl$ and the X-ray crystal structure of the monolithiate $[(TMEDA)Li(PhCH)_2PPh(CH_2Ph)]$ are reported, along with those of its complexes with Cp*Rh(III) and Cp*Cr(III) moieties.

2. Results and discussion

2.1. Lithiation studies of $[PhP(CH_2Ph)_3]Cl$

Treatment of phenyl tribenzylphosphonium chloride $[PhP(CH_2Ph)_3]Cl$ with three molar equivalents of ^{n}BuLi in THF results in the removal of three benzylic protons and formation of the orange dilithiated species $[Li_2PhP(CHPh)_3]$. Triple deprotonation was established by the observation that treatment of this species with excess MeI provides the trimethylated phosphonium salt $[PhP(CHMePh)_3]I$. This salt was characterised by mass spectrometry, with the successive loss of each methylated benzyl being observed, however NMR data was complicated by the presence of a mixture of diastereomers, although the phenyl and methyl signal integrals show the expected 20:9 ratio.

Addition of two equivalents of ^{n}butyllithium to a suspension of finely ground $[PhP(CH_2Ph)_3]Cl$ in THF-d_8 provides a solution whose NMR spectra indicate formation of the monolithiated (phosphoniodiylide) species $[LiPhP(CHPh)_2(CH_2Ph)]$ (**1**) (Fig. 2). The ^{13}C-^{31}P coupling constants observed in this system are of interest with coupling to the CH carbon atoms being much larger (124 Hz) than to the CH_2 carbon atom (44 Hz), a feature which we attribute to the increased interaction of the unsaturated carbon centres with the phosphorous, resulting in a large degree of delocalisation within the P–C bonds. Repeating this experiment using three molar equivalents of ^{n}butyllithium gives spectra that indicate the formation of the symmetrical dilithiated species $[Li_2PhP(CHPh)_3]$ (**2**) and which exhibit a ^{31}P-$^{13}CHPh$ coupling constant of 105 Hz.

Crystallisation of the dilithiate species **2** with the addition of various quantities of TMEDA or HMPA to the THF solution to complex the lithium ions was attempted, however, spectroscopic data suggests that the crystalline material isolated in all cases contains the monolithiate **1** rather than the dilithiate **2**. An X-ray crystal structure determination of [**1**·TMEDA] was undertaken and the molecular structure is shown in Fig. 3 with significant bond lengths and angles detailed in Table 1. The lithium is four coordinate, chelated by both the TMEDA and the phosphoniodiylide ligand in a distorted tetrahedral geometry. The phosphoniodiylide system is coordinated not via both P-CHPh carbon atoms as might be anticipated, but rather through one of the CHPh carbon atoms and the *ipso–ortho* bond of the phenyl ring of the second CHPh group. The phosphorous bonds to the CHPh carbon atoms [P(1)–C(3) 1.712(3), P(1)–C(2) 1.743(3) Å] are significantly shorter than that to the uncoordinated benzylic methylene [P(1)–C(1) 1.845(3) Å], and the bonding in this unit is best interpreted in terms of a P(1)–C(3) double bond and a P(1)–C(2) single bond shortened by its polar nature. The chelate angle obtained by TMEDA at the lithium centre is as would be expected at 88.3(2)°, compared to that of the ligand bite-angle of 98.9(3)°, highlighting the extremely distorted tetrahedral environment of the lithium. The difference in the bond lengths of the two coordinated ligand units [Li–C(2) 2.158(6), Li–C(36) 2.639(6) Å] emphasises the difference between the two interactions. The difference between the ^{31}P chemical shift observed for **1** (-1.7 ppm) and **1**.TMEDA (35.8 ppm) is noteworthy and arises possibly as a result of the coordination of the Li by TMEDA rather than THF which will alter the Lewis acidity of this centre. The possibility that the Li is coordinated in a different manner in **1**, via the ylidic P=CHPh unit for example, cannot be excluded and the large chemical shift difference suggests that this may be the case.

2.2. Synthesis and characterisation of transition metal complexes

Treatment of the chloro-bridged dimer $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ with the dilithiate **2** in THF provides an orange solution from which a species, initially assumed to be $[(\eta\text{-}C_5Me_5)Rh\{\eta^3\text{-}(CHPh)_3PPh\}]$, was obtained. However, spectroscopic data show that the complex isolated contains a mono- rather than a dianionic ligand and as such, may be identified as the phospho-

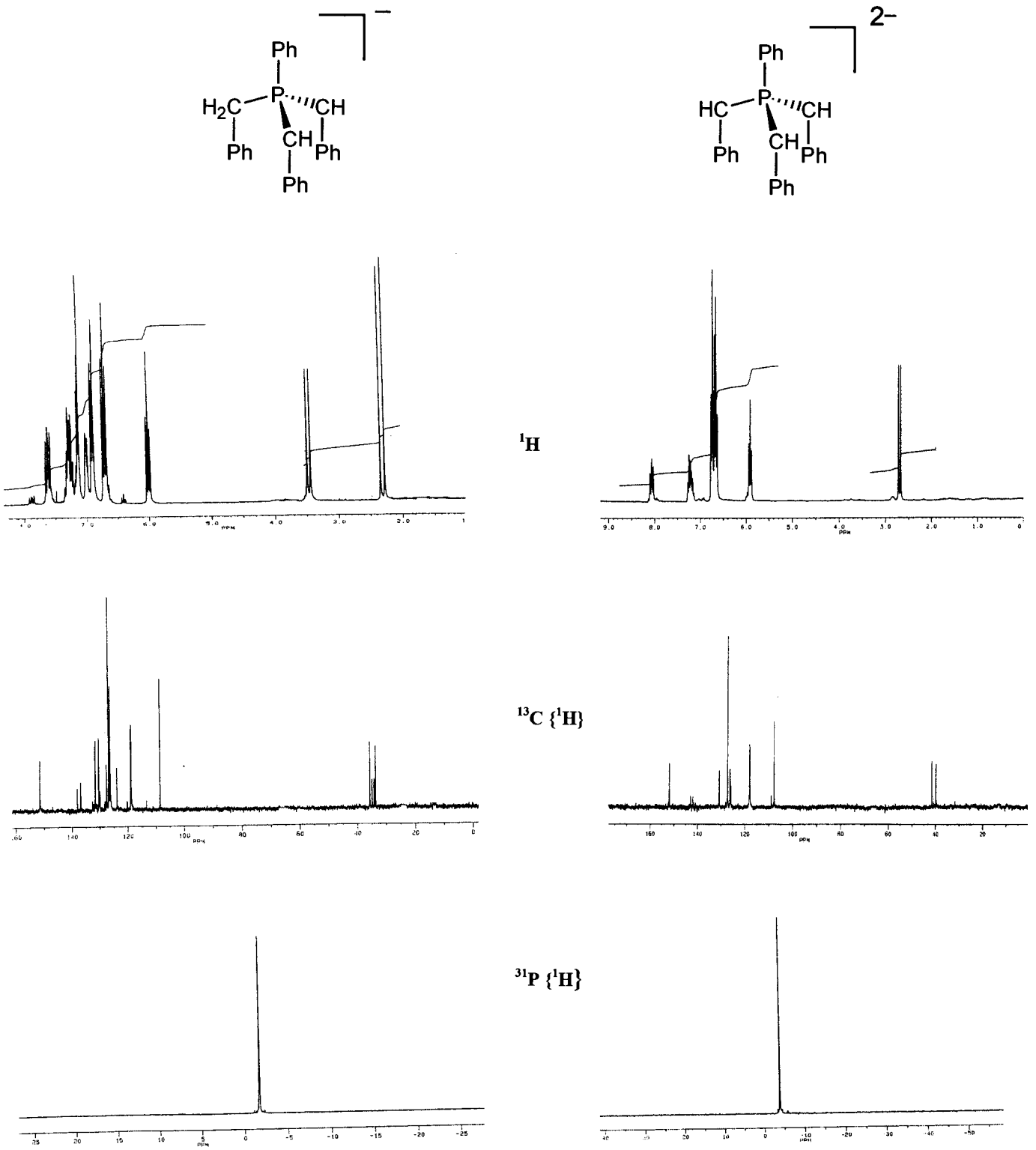

Fig. 2. NMR spectra of $[LiPhP(CHPh)_2(CH_2Ph)]$ (**1**) and $[Li_2PhP(CHPh)_3]$ (**2**) in THF-d_8.

niodiylide complex $[(\eta\text{-}C_5Me_5)Rh\{\eta^2\text{-}(CHPh)_2(CH_2Ph)PPh\}Cl]$ (**3**). Although this complex may be formed directly from the monolithiate **1**, we feel that, in light of the demonstrated formation of the ligand dianion above, its formation in the current instance is the result of the hydrolysis of the putative $[(\eta\text{-}C_5Me_5)Rh\{\eta^3\text{-}(CHPh)_3PPh\}]$ followed by the re-coordination of chloride, presumably present as LiCl which has a small but

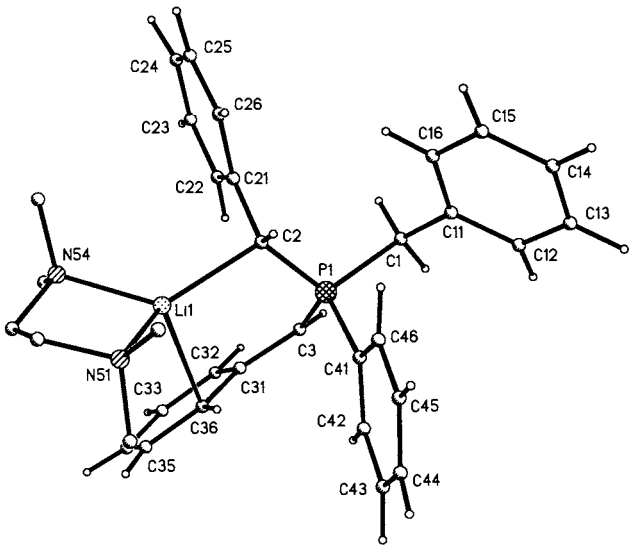

Fig. 3. Molecular structure of [(TMEDA)LiPhP(CHPh)$_2$(CH$_2$Ph)] (**1**·TMEDA).

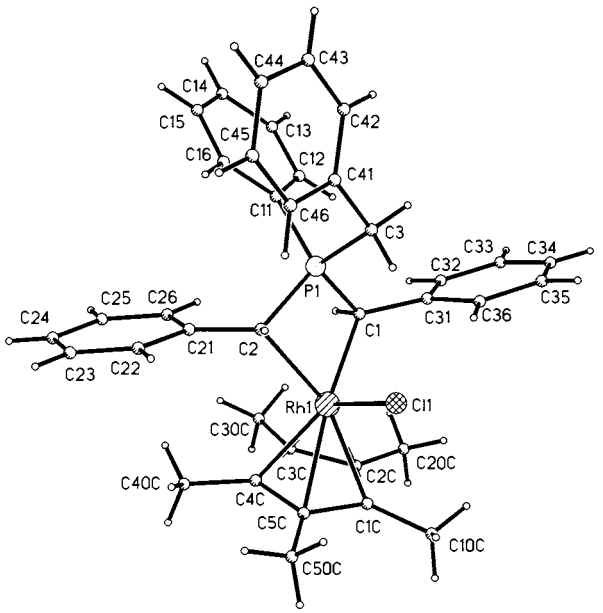

Fig. 4. Molecular structure of [(η-C$_5$Me$_5$)Rh{η^2-(CHPh)$_2$-PPh(CH$_2$Ph)}Cl] (**3**).

significant solubility in THF, to the resulting cationic species. This assumption is supported by the fact that, although lithiation of **3** may be effected by ^{n}BuLi, as evidenced by a colour change from red to green, all attempts at isolation of the resulting species lead only to the recovery of **1**.

An X-ray crystal structure determination of **3** was undertaken and the molecular structure is shown in Fig. 4 and significant bond lengths and angles are provided in Table 1. The diylide ligand chelates the rhodium with a bite-angle of 77.1(3)°, and the

Table 1
Selected bond lengths (Å) and angles (°) for **1**·TMEDA, **3** and **4**

1·TMEDA		**3**		**4**	
Bond lengths					
Li–N(54)	2.055(6)	Rh(1)–C(1)	2.166(7)	Cr(1)–C(3)	2.203(9)
Li–N(51)	2.126(6)	Rh(1)–C(2)	2.184(7)	Cr(1)–C(2)	2.169(8)
Li–C(2)	2.158(6)	Rh(1)–Cl(1)	2.4507(18)	Cr(1)–Br(1)	2.4606(19)
Li–C(36)	2.639(6)	P(1)–C(1)	1.762(7)	P(1)–C(1)	1.818(9)
Li–C(53)	2.730(6)	P(1)–C(2)	1.7775(18)	P(1)–C(2)	1.802(8)
P–C(3)	1.712(3)	P(1)–C(3)	1.824(7)	P(1)–C(3)	1.776(9)
P–C(2)	1.743(3)	P(1)–C(11)	1.806(7)	P(1)–C(41)	1.821(9)
P–C(41)	1.827(3)				
P–C(1)	1.845(3)				
C(1)–C(11)	1.506(4)				
C(2)–C(21)	1.458(4)				
C(3)–C(31)	1.421(4)				
Bond angles					
N(54)–Li–N(51)	88.3(2)	C(1)–Rh(1)–C(2)	77.1(3)	C(3)–Cr(1)–C(2)	78.7(3)
C(2)–Li–C(36)	98.9(2)	C(1)–P(1)–C(2)	100.0(3)	C(1)–P(1)–C(2)	110.6(4)
N(51)–Li–C(36)	106.3(2)	C(1)–P(1)–C(11)	113.7(3)	C(1)–P(1)–C(41)	105.1(4)
N(54)–Li–C(2)	129.9(3)	C(2)–P(1)–C(11)	115.6(3)	C(2)–P(1)–C(41)	114.6(4)
C(3)–P–C(2)	116.79(14)	C(1)–P(1)–C(3)	111.6(3)	C(1)–P(1)–C(3)	109.9(4)
C(3)–P–C(41)	103.46(13)	C(2)–P(1)–C(3)	111.2(3)	C(2)–P(1)–C(3)	101.6(4)
C(2)–P–C(41)	103.46(13)	C(11)–P(1)–C(3)	104.9(3)	C(41)–P(1)–C(3)	115.2(4)
C(3)–P–C(1)	102.84(14)				
C(2)–P–C(1)	112.74(15)				
C(41)–P–C(1)	107.49(13)				
P–C(2)–Li	108.9(2)				
P–C(3)–C(31)	126.2(2)				

C(1)–P(1)–C(2) angle at phosphorus is 100.0(3)°. With the exception of C(11)–P(1)–C(3) [104.9(3)°], the remaining angles at phosphorus are correspondingly increased from tetrahedral and range from 111.2(3) to 115.6(3)°. These distortions are less severe than those observed for a ruthenium complex of a nitrogen donor analogue of this ligand which we have recently reported [11], reflecting the greater atomic size of carbon. The phosphorus bonds to the metal coordinated carbon atoms [P(1)–C(1) 1.762(7), P(1)–C(2) 1.775(8) Å] are significantly shorter than that to the uncoordinated benzylic methylene [P(1)–C(3) 1.824(7) Å] indicating the heteroallylic nature of the coordinated unit. Significantly, the phenyl groups bonded to the coordinated carbon atoms are arranged *trans* with respect to the C(1)–C(2) vector as would be required in a C_3 symmetric η^3-coordinated ligand, and furthermore the uncoordinated benzyl group adopts the correct orientation for such a coordination symmetry.

Treatment of the bromo-bridged dimer $[(\eta\text{-}C_5Me_5)CrBr_2]_2$ with **2** in THF provides a deep green solution. Removal of the THF under vacuum leaves a green residue, which is readily redissolved in ether resulting in the formation of a white precipitate of LiBr. Cooling of this solution to −30°C for several days provides a crop of blue crystals from the green solution. X-ray crystal structure analysis reveals the structure to be that of the phosphoniodiylide complex $[(\eta\text{-}C_5Me_5)Cr\{\eta^2\text{-}(CHPh)_2PPh(CH_2Ph)\}Br]$ (**4**). The molecular structure of **4** is shown in Fig. 5 and significant bond lengths and angles are given in Table 1. The cyclopentadienyl ring is bound in a symmetrical η^5-fashion with Cr–C_{ring} distances in the range of [2.240–2.280 Å]. The two Cr–C bond distances to the chelating

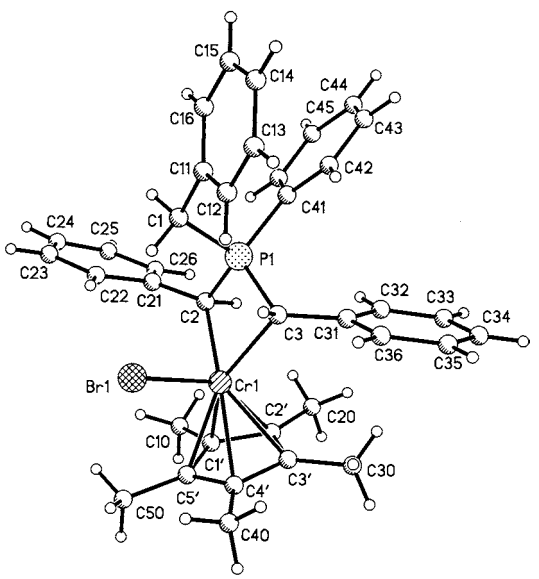

Fig. 5. Molecular structure of $[(\eta\text{-}C_5Me_5)Cr\{\eta^2\text{-}(CHPh)_2PPh(CH_2Ph)\}Br]$ (**4**).

phosphoniodiylide ligand do not differ significantly [Cr–C(2) = 2.169(8), Cr–C(3) = 2.203(9) Å] and all P–C bond lengths are likewise not distinguishable on the basis of crystallographic data, ranging from 1.776(9) to 1.818(9). The diylide chelates the chromium with a bite angle of 78.7(3)° and the C(2)–P(1)–C(3) angle at phosphorous is 101.6(4)°, with the remaining angles around the phosphorous ranging from 105 to 115°, indicating a minor distortion from tetrahedral geometry.

Phosphoniodiylide ligands $[R_2P(CR_2)_2]^-$ exhibit a preference for a $(\mu_2\text{-}\eta^2\text{-})$ bridging mode of coordination and have a particular affinity for Au(I) [12], although examples of the bridging of other metal dimers by phosphoniodiylides are also known, e.g. $[Mo_2\{(\mu_2\text{-}\eta^2\text{-}CH_2)_2PMe_2\}_4]$ [13]. In comparison, relatively few examples of complexes containing chelating phosphoniodiylide ligands have been characterised [14], and the Rh and Cr species reported here are, to our knowledge, the first such complexes for these metals [15].

In an attempt to obtain the η^3-coordinated ligand, the chelate complex **4** was dissolved in THF to obtain a blue solution and addition of 1 equivalent of ^{n}BuLi was carried out at −78°C. On warming the solution slowly to room temperature a deep green colour resulted, indicating that the third arm of the ligand has been successfully deprotonated. However, only a blue precipitate could be obtained from the resulting solution, which elemental analysis confirmed to be the starting phosphoniodiylide complex **4**, and it must therefore be assumed that the coordination of the third benzylic carbon, if it occurs at all, is only weak.

Our lithiation–methylation and NMR studies have shown that $[PhP(CHPh)_3Li_2]$ (**2**) is formed on treatment of the phosphonium salt with 3 molar equivalents of ^{n}BuLi, and the isolation of phosphoniodiylide complexes from the reaction of this species with the halide complexes $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ and $[(\eta\text{-}C_5Me_5)CrBr_2]_2$ must therefore be assumed to be due to the hydrolytic instability of the desired species $[(\eta\text{-}C_5Me_5)M\{\eta^3\text{-}(CHPh)_3PPh\}]$ due to the inability of this system to act as an effective tridentate ligand. In our studies of the analogous nitrogen donor ligand system $[(NR)_2PPh(NHR)]^-$, for which we found a similar inability to coordinate in an η^3-mode, we were able to attribute this failure to the electronic stabilisation of the unsaturated metal centre by strong π-donation by the chelating ligand, thus destabilising the η^3-mode relative to the chelating mode of coordination [11]. However, the carbon donors of the chelating $[(CHPh)_2PPh(CH_2Ph)]^-$ phosphoniodiylide ligand are incapable of π-donation and such an explanation is thus not valid for this ligand. We must therefore attribute our inability to isolate the complexes containing η^3-$(CHPh)_3PPh$ ligands by removal of HX from $[(\eta\text{-}C_5Me_5)M\{\eta^2\text{-}PhP(CH_2Ph)(CHPh)_2\}X]$ to the angle strain involved in

forming the three M-C–P–C 4-membered rings necessary in such a process. However, electronic factors must also be important as such angle strain does not prevent the trimethylenemethane ligand $[C(CH_2)_3]^{2-}$ from forming stable complexes in an η^3-coordination mode.

3. Experimental

3.1. General

All reactions were carried out under an atmosphere of dry, oxygen free nitrogen using standard Schlenk techniques and solvents which were dried and distilled under nitrogen immediately prior to use. The phosphonium salt $[PhP(CH_2Ph)_3]Cl$ was prepared by treatment of phenyl dibenzyl phosphine (from $PhPCl_2$ and benzyl magnesium chloride) with benzyl chloride, while $[\{(\eta\text{-}C_5Me_5)RhCl_2\}_2]$ and $[\{(\eta\text{-}C_5Me_5)CrBr_2\}_2]$ were prepared by the literature procedures [16,17]. NMR spectra were recorded on a Bruker AC 250 spectrometer and infrared spectra on a Perkin–Elmer Paragon 1000 spectrometer from samples as KBr discs. Mass spectra were recorded on a Kratos MS50 TC instrument in positive ion FAB mode using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Elemental analyses were conducted by the microanalytical service of this department.

3.2. Synthesis of [PhP(CHMePh)$_3$]I

Finely ground $[PhP(CH_2Ph)_3]Cl$ (0.50 g, 1.20 mmol) was suspended in THF (25 cm^3) with rapid magnetic stirring and ^{n}BuLi (2.25 cm^3 of a 1.6 M solution in hexane, 3.6 mmol) was slowly added by syringe under nitrogen. After stirring for 1 h, methyl iodide (0.25 cm^3, 4.01 mmol) was added by syringe. After a further 15 min 50 cm^3 of water was added and the mixture extracted with CH_2Cl_2 (3×20 cm^3). Crystallisation provided the product as a colourless microcrystalline material (0.46 g, 70%). ^{1}H-NMR ($CDCl_3$): complex set of overlapping multiplets due to a mixture of diastereoisomers; MS (+FAB): 423 (M^+), 319 ($M^+ -$ CHMePh), 213 ($M^+ - 2$CHMePh), 105 (CHMePh).

3.3. Preparation of [Li(CHPh)$_2$(CH$_2$Ph)PPh] (1) and [Li$_2$(CHPh)$_3$PPh] (2) for NMR studies

The solvent was removed from the required volume of ^{n}butyllithium in hexane (1.6 M) in vacuo in a 5 mm NMR tube. Deuterated THF (0.5 cm^3) was then added to the resultant powder at −30°C before addition of either 0.5 (for **1**) or 0.33 (for **2**) molar equivalents of $[PhP(CHPh)_3]Cl$. The NMR tube was sealed and the mixture was allowed to warm to room temperature (r.t.) for 30 min with occasional shaking. The NMR spectra were recorded from the resultant clear solutions.

Data for **1**: ^{1}H-NMR (250 MHz, THF-d_8): δ 5.8–7.9 (mult, 20H, Ph), 3.55 (d, $J_{H-P} = 13$ Hz, 2H, CH_2), 2.29 (d, $J_{H-P} = 17$ Hz, 2H, CH); ^{13}C-NMR (62.9 MHz, THF-d_8): δ 151.4 (d, quat, $J_{C-P} = 32.0$ Hz, P–Ph), 138.0 (d, quat, $J_{C-P} = 15.0$ Hz, CH–*Ph*), 136.7 (d, quat, $J_{C-P} = 4.0$ Hz, CH_2–*Ph*), 9 other peaks between 108–141 (Ph), 34.6 (d, $J_{C-P} = 124$ Hz, CH), 34.3 (d, $J_{C-P} = 45.0$ Hz, CH_2); ^{31}P-NMR (101.2 MHz, THF-d_8) δ −1.7.

Data for **2**: ^{1}H-NMR (250 MHz, THF-d_8): δ 5.9 (mult, Ph), 6.7 (mult, Ph), 7.2 (mult, Ph), 8.1 (mult, Ph), 2.6 (d, $J_{H-P} = 11.2$ Hz, 3H, C*H*). ^{13}C-NMR (62.9 MHz, THF-d_8): δ 142.3 (d, $J_{C-P} = 61.0$ Hz, P–Ph), 117.8 (d, $J_{C-P} = 12.0$ Hz, P–Ph), 130.7 (d, $J_{C-P} = 9.5$ Hz, P–Ph), 126.1 (d, $J_{C-P} = 8.0$ Hz, P–Ph), 151.7 (d, $J_{C-P} = 4.0$ Hz, CH–*Ph*), 127.2 (CH–*Ph*), 108.8 (CH–*Ph*), 105.1 (CH–*Ph*), 40.4 (d, $J_{C-P} = 105$ Hz, CH). ^{31}P-NMR (101.2 MHz, THF-d_8) δ −3.9.

3.4. Synthesis of [(TMEDA)Li(CH$_2$Ph)(CHPh)$_2$PPh] (1·TMEDA)

To a suspension of $[PhP(CH_2Ph)_3]Cl$ (0.20 g, 0.481 mmol) in ether, ^{n}BuLi (1.6 M solution in hexane) (0.90 cm^3, 1.442 mmol) and TMEDA (0.15 cm^3, 0.962 mmol) were added at −78°C. The reaction mixture was allowed to warm to r.t. and stirred for 2 h. The bright red solution obtained was filtered through celite and the resultant clear filtrate reduced to half its original volume. After leaving this solution for 10 h at −30°C, yellow crystals of **1** were obtained in 78% yield. Elemental analysis: Anal. Found C, 79.13; H, 7.69; N, 5.92; $C_{33}H_{40}N_2PLi$ requires C, 78.85; H, 8.04; N, 5.58%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.1–7.6 (mult, 19H, Ph), 3.3 (d, $J_{H-P} = 14.0$ Hz, 4H, CH_2–P), 2.4 (4H, CH_2–N), 2.2 (12 H, CH_3–N), 2.1 (d, $J_{H-P} = 12.0$ Hz, 1H, CH–P).); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ 125–135 (Ph), 45.6 (CH_3–N), 57.4 (CH_2–N), 29.5 (quat, Ph–Li), 37.2 (d, $J_{P-C} = 63.5$ Hz, P–CH_2), 326.2 (d, $J_{P-C} = 64$Hz, CH–P); ^{31}P-NMR (101.2 MHz, $CDCl_3$): δ 35.8.

3.5. Synthesis of [(η-C$_5$Me$_5$)Rh{η^2-(CHPh)$_2$PhP(CH$_2$Ph)}Cl] (3)

Finely ground $[PhP(CH_2Ph)_3]Cl$ (0.825 g, 1.98 mmol) was suspended in THF (25cm^3) with rapid magnetic stirring and ^{n}BuLi (3.72 cm^3 of a 1.6 M solution in hexane, 5.95 mmol) was slowly added by syringe under nitrogen. After stirring for 1 h $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ (0.611 g, 0.99 mmol) was added to the orange solution and allowed to stir overnight upon which the reaction mixture had become deep red in colour. The solvent was removed in vacuo and the red residue redissolved

Table 2
Crystal data for **1**·TMEDA, **3** and **4**

	1·TMEDA	**3**	**4**
Empirical formula	$C_{35.25}H_{45.25}LiN_2P$	$C_{37}H_{39}ClPRh$	$C_{37}H_{39}CrPBr$
Formula weight	534.89	635.01	646.56
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P21/c$	$P2_1/c$	$P21/c$
a (Å)	9.6393(9)	10.685(6)	10.645(4)
b (Å)	16.9065(15)	19.349(7)	19.381(10)
c (Å)	19.852(2)	15.194(4)	15.325(7)
β (°)	92.382(8)	93.67(3)	94.04(6)
V (Å^3)	3232.4(5)	3135(2)	3154(3)
Z	4	4	4
Temperature (K)	220(2)	200(2)	150(2)
Crystal habit	Orange block	Red block	Blue plate
Crystal size (mm)	$0.58 \times 0.39 \times 0.23$	$0.23 \times 0.23 \times 0.23$	$0.57 \times 0.23 \times 0.08$
Wavelength (Å)	1.54184	0.71073	1.54184
2θ range (°)	5–140	5–50	5–140
D_{calc} (Mg m^{-3})	1.099	1.384	1.326
μ(Mo–K$_\alpha$) (mm^{-1})	0.919	0.705	5.115
Transmission range	0.311–0.417	0.834–0.864	0.355–0.761
Number of parameters	474	367	366
R_1 (Number of data with $F>4\sigma(F)$]	0.0655 (4219)	0.0632 (3097)	0.0929
wR_2 (all data)	0.1906 (5933)	0.1299 (5547)	0.2852
Final difference map (eÅ^{-3})	−0.35 to +0.45	−0.81 to +0.61	−1.64 to +2.05

in ether, filtered through celite and passed through a dry flash column using EtOAc as eluent. The solvent was then allowed to evaporate slowly resulting in dark red crystals of compound **1** (32%). Elemental analysis: Anal. Found: C, 68.7; H, 6.01; $C_{37}H_{39}ClPRh$ requires C, 68.0; H, 5.97%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.1 (s, 15H, Cp*CH_3), 2.8 [dd, 1H, HCHPh, $^2J(^1$H-^{31}P) = 13.5 Hz, $^2J(^1$H-^{1}H) = 10.0 Hz], 3.2 [dd, 1H, RhCH, $^1J(^1$H-^{31}P) = 8.5, $^2J(^1$H-^{103}Rh) = 3.0 Hz], 3.3 [dd, 1H, RhCH, $^1J(^1$H-^{31}P) = 7.0, $^2J(^1$H-^{103}Rh) = 3.0 Hz], 5.7 [dd, 1H, HCHPh, $^2J(^1$H-^{31}P) = 14.0, $^2J(^1$H-^{1}H) = 12.0 Hz], 6.5–8.0 (m, 20H, ArH). ^{13}C-NMR (62.89 MHz, $CDCl_3$): δ −7.1 [dd, RhCP, $^1J(^{13}$C-^{31}P) = 43.0, $^2J(^{13}$C-^{103}Rh) = 23.0 Hz], −3.7 [dd RhCP, $^1J(^{13}$C-^{31}P) = 52.5, $^2J(^{13}$C-^{103}Rh) = 18.5 Hz], 7.9 (Cp*CH$_3$), 31.7 [d, CH$_2$, $^1J(^{13}$C-^{31}P) = 40.0 Hz], 94.0 [d, Cp*, quat$C$, $^1J(^{13}$C-^{103}Rh) = 6.5 Hz], 135.2, 135.7 (RhCHPh, quat$C$), 140.5 [d, PPh, quat$C$, $^1J(^{13}$C-^{31}P) = 6.5 Hz], 144.2 (CH$_2$Ph, quat$C$). ^{31}P-NMR (101.26 MHz, $CDCl_3$): δ 37.8 [d, $^2J(^{31}$P-^{103}Rh) = 27.0 Hz). MS (+FAB): m/z = 617 (M$^+$), 447, 380, 289, 237, 154, 77.

3.6. Synthesis of [(η-C$_5$Me$_5$)Cr{η^2-(CHPh)$_2$PhP(CH$_2$Ph)}Br] (4)

Finely ground [PhP(CH$_2$Ph)$_3$]Cl (0.20 g, 0.480 mmol) was suspended in THF (25 cm^3) and ^{n}BuLi (0.90 cm^3, 1.44 mmol, 1.6 M solution in hexane) was added at −78°C. The solution was allowed to warm to r.t. and then recooled to −78°C. To the resulting red solution was added [Cp*CrBr$_2$]$_2$ (0.166 g, 0.240 mmol), rewarming to r.t. provided a green solution. Removal of the solvent in vacuo and dissolution of the resulting residue in ether gave a similar deep green solution with a small amount of white precipitate which was identified as LiBr by $AgNO_3$ and flame tests. Filtration of this solution through a pad of celite, reduction in the volume of ether and storing of the solution at −30°C overnight resulted in the formation of blue crystals (0.160 g, 52%). These were found to be of insufficient quality for X-ray diffraction analysis. The solution was then re-filtered through celite and the resulting solution was stored at 5°C. After one week the solution afforded a crop of blue crystals suitable for X-ray diffraction analysis. Elemental analysis: Anal. Found C, 68.61; H, 6.13; N, 0; $C_{37}H_{39}PClCr$ requires C, 68.72; H, 6.09; N, 0%.

4. X-ray crystallography

All data collections were performed on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device. Structures **1**·TMEDA and **3** were solved by direct methods (SIR92 [18]), structure **4** was solved by Patterson methods (DIRDIF [19]); all refinements were performed against F^2 (SHELXL97 [20]). The absorption correction for **1**·TMEDA was performed using ψ-scan data; those for **3** and **4** were performed by Gaussian integration following refinement of the crystal shape and dimensions against a set of ψ-scans (Stoe X-Shape [21]). Crystal and refinement

data are given in Table 2. The structure of **1**·TMEDA contained a disordered hexane molecule in the region of a crystallographic inversion centre. The H atoms incorporated in the phosphoniodiylide were located in a difference map and refined freely, methyl groups were treated as rotating rigid bodies and all other H atoms are in idealised positions. All non-H atoms with the exception of the minor solvent component were refined anisotropically. Refinement of the crystal structure of **3** presented no major problems. H atoms attached to C1, C2 and C3 were located in difference maps, but are included in idealised positions, CH_3 groups were treated as rotating rigid bodies, and all other H positions were calculated. All non-H atoms were modelled with anisotropic displacement parameters. Crystals of **4** were of rather low quality, being mostly small and clustered. The crystal selected was a plate with another small crystal attached to the prominent growth face (100), but it was not possible to dissect the crystal clusters without completely fragmenting the sample. $Cu–K_\alpha$ radiation was used for data collection for its higher intensity and scattering efficiency relative to $Mo–K_\alpha$ radiation, although absorption effects were fierce. The resulting crystal structure is therefore of low precision, and while it confirms connectivity (note the isostructural relationship with **3**) it is not of sufficient quality for detailed analysis. H positions were all calculated; all non-H atoms were refined anisotropically. Twinning via 180° rotation about (001) would predominantly affect data where 0.1 *l* is near integral; omitting these data reduces the final difference map residuals to ± 1.3 eÅ^{-3}, but only reduces R_1 to 8.8%. Improvements of a similar order of magnitude could be obtained using a calculated absorption correction (SHELXA), and so the high *R* factor and noisy difference map could also be due to residual absorption errors. Both these effects are neglected in the data presented here.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 151 738, 151 739 and 151 740 for compounds **1**·TMEDA, **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Engineering and Physical Science Research Council (EPSRC) for a project studentship (to T.B.) and provision of a 4-circle diffractometer.

References

[1] (a) M.D. Jones, R.D.W. Kemmitt, Adv. Organomet. Chem. 27 (1987) 279 and references therein. (b) R.S. Lokey, N.S. Mills, Organometallics, 8 (1989) 1803. (c) G.E. Herberich, U. Englert, L. Wesemann, P. Hofmann, Angew. Chem. Int. Ed. Engl. 30 (1991) 313. (d) G.E. Herberich, T.P. Spaniol, J. Chem. Soc., Chem. Commun. (1991) 1457. (e) G.E. Herberich, T.P. Spaniol, J. Chem. Soc., Dalton Trans. (1993) 2471. (f) I.-Y.Wu, M.-C. Cheng, Y.-C. Lin, Y. Wang, Organometallics, 12 (1993) 1686.
[2] G.E. Herberich, C. Kreuder, U Englert, Angew. Chem. Int. Ed. Engl. 33 (1993) 2465.
[3] (a) G.C. Bazan, G. Rodriguez, B.P. Cleary, J. Am. Chem. Soc. 116 (1994) 2177. (b) G. Rodriguez, G.C. Bazan, J. Am. Chem. Soc. 117 (1995) 10155.
[4] B.M. Trost, Angew. Chem. Int. Ed. Engl. 25 (1986) 1 and references therein.
[5] P.J. Bailey, A.J. Blake, M.J. Kryszczuk, S. Parsons, D. Reed, J. Chem. Soc. Chem. Commun. (1995) 1647.
[6] (a) M.J. Burk, R.L. Harlow, Angew. Chem Int. Ed. Engl. 29 (1990) 1462. (b) T.R. Ward, L.M. Venanzi, A. Albinati, F. Lianza, T. Gerfin, V. Gramlich, G.M.R. Tombo, Helv. Chim. Acta 74 (1991) 983. (c) M.J. Burk, J.E. Feaster, R.L. Harlow, Tet. Asym. 2 (1991) 569. (d) W.A. Nugent, J. Am. Chem. Soc. 114 (1992) 2786. (e) C.J. Tokar, P.B. Kettler, W.B. Tolman, Organometallics 11 (1992) 2737. (f) H. Adolfsson, K. Warnmark, C. Moberg, J. Chem. Soc.Chem. Commun. (1992) 1054. (g) D.D. LeCloux, W.B. Tolman, J. Am. Chem. Soc. 115 (1993) 1153. (h) D.D. LeCloux, C.J. Tokar, M. Osawa, R.P. Houser, M.C. Keys, W.B. Tolman, Organometallics 13 (1994) 2855. (i) W.A. Nugent, R.L. Harlow, J. Am. Chem. Soc. 116 (1994) 6142. (j) B.S. Hammes, D. Ramos-Maldonado, G.P.L. Yap, L. Liable-Sands, A.L. Rheingold, V.G. Young Jr., A.S. Borovik, Inorg. Chem. 36 (1997) 3210. (k) C. Bolm, D. Kadereit, M. Valacchi, Syn. Let. (1997) 687.
[7] C. Moberg, Angew. Chem. Int. Ed. Engl. 37 (1998) 248.
[8] J.K. Whitesell, Chem. Rev. 89 (1989) 1581.
[9] (a) P.J. Bailey, L.A. Mitchell, S. Parsons, J. Chem. Soc. Dalton. Trans. (1996) 2839. (b) P.J. Bailey, R.O. Gould, C.N. Harmer, S. Pace, A. Steiner, D.S. Wright, Chem. Commun. (1997) 1161. (c) M.B. Dinger, W. Henderson, J. Chem. Soc. Chem. Commun. (1996) 211. (d) S.D. Robinson, A. Sahajpal, J. Chem. Soc. Dalton Trans. (1997) 3349. (e) J.R. da, S. Maia, P.A. Gazard, M. Kilner, A.S. Batsanov, J.A.K. Howard, J. Chem. Soc. Dalton Trans. (1997) 4625. (f) P.J. Bailey, S.F. Bone, L.J. Yellowlees, L.A. Mitchell, S. Parsons, K.J. Taylor, Inorg. Chem. 36 (1997) 867. (g) P.J. Bailey, S.F. Bone, L.J. Yellowlees, L.A. Mitchell, S. Parsons, K.J. Taylor, Inorg. Chem. 36 (1997) 5420.
[10] P.J. Bailey, S. Pace, Coord. Chem. Rev. 214 (2001) 91.
[11] P.J. Bailey, K.J. Grant, S. Parsons, Organometallics 17 (1998) 551.
[12] (a) H. Schmidbaur, Acc. Chem. Res. 8 (1975) 113. (b) H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 15 (1976) 728. (c) H. Schmidbaur, Pure Appl. Chem. 50 (1978) 19.
[13] F.A. Cotton, B.E. Hanson, W.H. Ilsley, G.W. Rice, Inorg. Chem. 18 (1979) 2713.
[14] (a) D.J. Brauer, C. Kruger, P.J. Roberts, Y.-H. Ssay, Chem. Ber. 107 (1974) 3706. (b) J.-M. Bassett, J.R. Mandt, H. Schmidbaur, Chem. Ber. 113 (1980) 1145. (c) H. Schmidbaur, A. Moetl, B. Zimmer-Gasser, Chem. Ber. 114 (1981) 3161. (d) G.W. Rice, G.B. Ansell, M.A. Modrick, S. Zentz, Organometalics 2 (1983) 154. (e) J.P. Fakler, B. Trzcinska-Bancroft, Organometallics 4 (1985) 1891. (f) E.J. More, B.D. Santarsiero, Acta Crystallogr. Sect. C 44 (1988) 1911. (g) M. Gomez, G. Jimenez, P. Royo, M.A. Pellinghelli, A. Tiripicchio, J. Organomet. Chem. 439 (1992) 309. (h) M.J. Hostetler, M.D. Butts, R.G. Bergman, Inorg. Chim. Acta 198 (1992) 377.

[15] Cambridge Structural Database search, issue 20, October 2000.
[16] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228.
[17] F.H. Kohler, J. Lachmann, G. Muller, H. Zeh, H. Bruneer, J. Wachter, J. Organomet. Chem. 365 (1989) C15.
[18] (a) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343. (b) Stoe X-Shape–Stoe & Cie, X-Shape, Darmstadt, Germany, 1998.
[19] P.T. Beurskens, G. Beurskens, W.P. Bosman, R. de Gelder, S. Garcia-Granda, R.O. Gould, R. Israel, J.M.M. Smits, Crystallography Laboratory, University of Nijmegen, The Netherlands. 1996.
[20] G. M. Sheldrick, SHELX 97 & SHELXA Programs for Crystal Structure Analysis (Release 97-2), Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
[21] Stoe X-Shape–Stoe & Cie, X-Shape, Darmstadt, Germany, 1998.