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Synthesis and characterisation of a novel nickel trihydride. Crystal structure of $[\{Ni(dippe)\}_2H_3][BPh_4]$ (dippe = $Pr^i_2PCH_2CH_2PPr^i_2$)

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The reaction of anhydrous $NiBr_2$ with 1,2-bis(diisopropylphosphino)ethane (dippe) in ethanol yielded the orange complex $[NiBr_2(dippe)]$ **1**. This compound reacted with $NaBH_4$ in ethanol to yield the dimeric trihydride $[\{Ni(dippe)\}_2H_3]^+$, isolable as its tetraphenylborate salt **2a**, for which the crystal structure has been determined. The structure suggests that there is one bridging hydride, the other two (one attached to each Ni) being terminal. An analogous complex containing the bulky phosphine 1,2-bis(dicyclohexylphosphino)ethane has also been prepared. These binuclear trihydrides are non-rigid and undergo rapid scrambling of the hydride ligands in solution even at −85 °C. All the compounds were characterised by IR and NMR spectroscopy and microanalysis.

Hydride complexes of nickel have been known for a long time.[1] Most contain terminal hydride ligands, and are of the type *trans*-$[NiH(X)(PR_3)_2]$ (X = halide, O_2CMe, OPh, pyrrol-1-yl, CN, Me or Ph; R = alkyl or aryl).[2–5] Analogous complexes with bidentate phosphines are unknown, as far as we are aware, possibly because a *cis* stereochemistry is implied, and this may eventually lead to reductive elimination of HX. However, compounds containing tripodal phosphine ligands, such as $[NiH(L)]^+$ [L = $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$],[6] are known. Some of these complexes are considered as models not only for hydrogenation catalysts, but also for Ziegler–Natta catalysis.[7] In contrast with terminal hydride complexes of nickel, which are relatively abundant, there are rather few examples of stable nickel derivatives containing bridging hydride ligands. The earliest reports correspond to complexes of the type $[\{Ni(R_2P(CH_2)_nPR_2)\}_2(\mu\text{-}H)_2]$ (n = 2–4, R = C_6H_{11} or Ph).[7–9] Other interesting examples are the anionic binuclear monohydrides $[\{Ni(C_2H_4)_2\}_2(\mu\text{-}H)]^-$ [10] and $[\{Ni(CO)_3\}_2(\mu\text{-}H)]^-$ [11] There are also tri- and tetra-nuclear nickel clusters in which the metal atoms are bridged by μ_3-hydride ligands, such as $[\{Ni(C_5H_3Bu^t_2)\}_3(\mu_3\text{-}H)_2]$ [12] or $[\{Ni(C_5H_5)\}_4(\mu_3\text{-}H)_3]$.[13] Many of these compounds have been subjected to X-ray analysis,[7,10–13] and even neutron diffraction.[14] However, all other reports concerning nickel complexes with bridging hydride ligands correspond, as far as we are aware, to heterobimetallic species, *e.g.* $[Ni(OC)_3(\mu\text{-}H)\text{-}Nb(C_5H_5)_2(CO)]$.[15]

Our research group has been exploring the reactivity of complexes of Fe, Mo and Ru containing the bulky, strongly electron-releasing diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe), and we became interested in the study of its nickel complexes. Several alkene and alkyne nickel(0)-dippe adducts have been reported,[16] as well as the dialkyls $[NiR_2(dippe)]$ (R = $CH_2C_6H_4Me$-*o* or CH_2SiMe_2Ph),[17] which are thermally very stable and do not undergo metallation reactions, at variance with the PMe_3 analogues.[18] No hydride complexes have been previously described. In this work, we report the synthesis, properties and crystal structure of the novel binuclear bridging trihydride $[Ni_2H_3(dippe)_2][BPh_4]$, as well as the preparation and properties of the related complex containing 1,2-bis(dicyclohexylphosphino)ethane (dcpe) as co-ligand.

Results and Discussion

The complex $[NiBr_2(dippe)]$ **1** (prepared by reaction of anhydrous $NiBr_2$ with dippe in ethanol) reacts smoothly with $NaBH_4$ in ethanol to yield brown solutions. Addition of $NaBPh_4$ produced a golden-yellow, crystalline precipitate, which can be recrystallised from acetone in the form of red-orange needles. These crystals become yellow and opaque on standing at room temperature even under an inert atmosphere. Decay can be avoided by storing this material in a freezer at −20 °C. This compound is diamagnetic, and its ^1H NMR spectrum $[(CD_3)_2CO]$ displays one quintet at δ −13.357, J_{HP} = 26.6 Hz, attributable to hydridic protons coupled to four equivalent phosphorus atoms. Since each starting nickel complex **1** contains only one phosphine ligand, the presence of a quintet suggests that a dimer containing two equivalent Ni(dippe) moieties has formed, having hydride ligands which may eventually act as bridges between the nickel atoms. The $^{31}P\text{-}\{^1H\}$ NMR spectrum consists of one sharp singlet at δ 97.3. These data, together with microanalysis, indicate a formula $[\{Ni(dippe)\}_2H_x][BPh_4]$, with an undetermined number x of hydride ligands. The value of x was established from the ^{31}P NMR spectrum, recorded with selective coupling to the hydride protons. In this fashion, the singlet observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum splits into a quartet (J_{PH} = 27 Hz), and therefore, the compound can be formulated as $[\{Ni(dippe)\}_2H_3]\text{-}[BPh_4]$ **2a**.

Table 1 Selected bond distances (Å) and angles (°) for $[\{Ni(dippe)\}_2\text{-}H_3][BPh_4]$

Ni–Ni	2.316(5)	Ni–H(1)	1.1(1)
Ni–P(1)	2.149(5)	Ni–H(2)	1.6(1)
Ni–P(2)	2.139(6)		
Ni–Ni–P(1)	131.3(2)	P(1)–Ni–H(1)	108(7)
Ni–Ni–P(2)	138.2(2)	P(1)–Ni–H(2)	140(1)
Ni–Ni–H(1)	54(6)	P(2)–Ni–H(1)	124(6)
Ni–Ni–H(2)	45(5)	P(2)–Ni–H(2)	103(4)
P(1)–Ni–P(2)	90.3(2)	H(1)–Ni–H(2)	96(7)

The dimeric nature of **2a** has been confirmed by X-ray analysis. An ORTEP[19] view of the trihydride cation is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. There are four cations $[\{Ni(dippe)\}_2H_3]^+$ and four anions $[BPh_4]^-$ in the unit cell. The asymmetric unit consists of half a cation and half an anion, with a two-fold axis passing through the midpoint of the Ni–Ni bond, and through H(2). The Ni–Ni bond length 2.316(5) Å is shorter than the sum of two metallic radii (2.492 Å), and also shorter than those found in other binuclear complexes of nickel containing tertiary phosphines as ligands, such as $[\{Ni(PMe_3)_2\}_2(\mu\text{-}AsBu^t_2)_2]$ (2.429 Å)[20] or

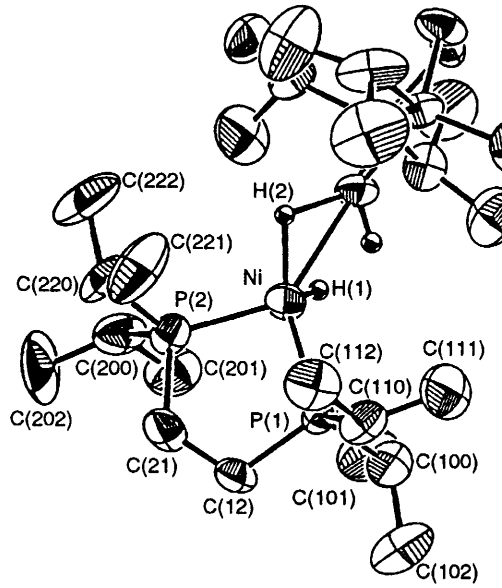

Fig. 1 An ORTEP drawing of the cation $[\{Ni(dippe)\}_2H_3]^+$ with 50% probability thermal ellipsoids. Hydrogen atoms, except hydrides, are omitted

$[\{Ni(PMe_3)_2\}_2(\mu\text{-}PBu^t{}_2)_2]$ (2.375 Å),[21] or even in hydrido-bridged species, *i.e.* $[\{Ni[(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2]\}_2(\mu\text{-}H)_2]$ (2.444 Å)[7] or $[Na(tmen)][\{Ni(C_2H_4)_2\}_2(\mu\text{-}H)]$ (tmen = $Me_2NCH_2CH_2NMe_2$) (2.596 Å).[10] These bond distances have been attributed to the presence of a single Ni–Ni bond in these compounds. The shortest Ni–Ni distances found in the literature correspond to the trinuclear cluster $[\{Ni(C_5H_3Bu^t{}_2)\}_3(\mu_3\text{-}H)_2]$,[12] which exhibits Ni–Ni separations between 2.337 and 2.349 Å, very similar to the value found for **2a**, but still slightly longer. The planes of the two NiP_2 units in the complex cation form a dihedral angle of 73.2°, having a geometry similar to that found in $[\{Ni[(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2]\}_2H_2]$,[7] and also in the closely related platinum complex $[\{Pt[Bu^t{}_2P(CH_2)_3PBu^t{}_2]\}_2H_3][BPh_4]$.[22a] The arrangement of the end fragments of the binuclear cation is a result of the bulky isopropyl substituents on phosphorus, and the short Ni–Ni bond causing these isopropyl groups to interlock into one another, as has been observed for the cobalt hydride $[\{Co[Pr^i{}_2P(CH_2)_3PPr^i{}_2]\}_2H_4]$.[23] The hydride atoms were located and refined, although their positions should be considered as tentative, so the result must be regarded with caution. Two hydrides appear as terminal, attached to each nickel atom, the third acting as a non-linear, symmetrical bridge between the two metal atoms. The terminal Ni–H(1) bond appears shorter than the bridging Ni–H(2), as expected. It is interesting to consider the effect of the hydride bridge on the Ni–Ni distance. For binuclear platinum complexes having both terminal and bridging hydride ligands it has been found that the Pt–Pt distance is strongly dependent on the number of hydride bridges.[22d] If this also applies to nickel, a Ni–Ni distance longer than in the complex $[\{Ni[(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2]\}_2H_2]$, which has two symmetrical bridging hydrides, should be expected for complex **2a**, which has only one hydride bridge. However, this is not the case. One possible reason for this could be that the steric requirements of the cyclohexyl groups of the phosphine ligand (bulkier than the isopropyl substituents of dippe) do not allow the nickel atoms to approach closer in this compound, resulting in a longer Ni–Ni separation. What is clear is that **2a** has a shorter Ni–Ni bond length than that expected for a binuclear nickel complex with only one symmetrical bridging hydride. The possibility of Ni–Ni multiple bonding in **2a**, accounting for the short Ni–Ni distance observed, cannot be discounted. Furthermore, the metal centres are not electronically saturated, and multiple metal–metal bonding might be a way of increasing the formal electron count.

From the crystal structure it is clear that the hydride atoms cannot be equivalent in a static structure. However, both hydride and phosphorus atoms are equivalent in solution, as inferred from the ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra. These spectra do not undergo any change when the sample is cooled to −85 °C, apart from a slight broadening in the signals which does not affect the splitting pattern. This means that complex **2a** is fluxional even at this temperature, and the hydride ligands undergo rapid scrambling in solution. There is no precedent for analogous cationic hydrides of nickel, but a series of platinum derivatives of the type $[\{Pt(L\text{–}L)\}_2H_3]^+$(L–L = diphosphine) have been reported.[22a–c] These are also fluxional even at low temperatures, in contrast with those having monodentate phosphine ligands $[\{Pt(PR_3)_2\}_2H_3]^+$ which are stereochemically rigid.[22d,e] Their IR spectra in solution and in the solid state display bands corresponding to both terminal and bridging hydride ligands, so the fluxionality has been interpreted in terms of exchange of the hydride atoms between terminal and bridging sites. Complex **2a** shows a broad IR (Nujol) band at 1673 cm^{-1}, which could be ascribed to a ν(NiHNi) vibration rather than to a terminal ν(NiH) stretching. However, the absence of ν(NiH) bands in the IR spectrum does not rule out completely the possibility that terminal hydride ligands might be present in **2a**. Our spectral data, and those reported for related platinum complexes, are consistent with the structure obtained by X-ray analysis (Fig. 1), in which one hydride acts as bridging and the other two are terminal, so **2a** should be formulated as $[\{NiH(dippe)\}_2(\mu\text{-}H)][BPh_4]$. The fluxional behaviour then arises from the rapid exchange between terminal and bridging positions, this interconversion being possible through the intermediacy of a transient species. This could be a complex having three bridging hydride ligands, namely $[\{Ni(dippe)\}_2(\mu\text{-}H)_3]^+$, although for the $[\{Pt(L\text{–}L)\}_2H_3]^+$ (L–L = diphosphine) system an intermediate involving a four- and five-coordinate platinum(II) pair of the type $[(L\text{–}L)PtH\text{–}PtH_2(L\text{–}L)]^+$, with no hydride bridges,[22] has been found to be more reasonable. Something similar may apply in our case, but since the barriers to these rearrangements seem to be very low the true nature of the transient species remains unclear.

We have also prepared the complex $[\{Ni(dcpe)\}_2H_3][BPh_4]$ **2b**, following a procedure analogous to that used for **2a**, starting from $[NiBr_2(dcpe)]$. The NMR spectra of **2b** are similar to those of **2a**, being also temperature independent, so an analogous structure and fluxional behaviour can be expected, which had never been described before despite the fact that the closely related derivative $[\{Ni(dcpe)\}_2(\mu\text{-}H)_2]$ was reported years ago.[7,8] Furthermore, the reaction of $[NiCl_2(dcpe)]$ with $LiBH_4$ in tetrahydrofuran (thf) had been described, the final product of this reaction being the nickel–boron complex $[\{Ni(dcpe)\}_2(\mu\text{-}BH_2)_2(\mu\text{-}H)_2]$, which gradually loses H_2 yielding $[\{Ni(dcpe)\}_2(\mu\text{-}BH_2)_2]$.[7] None of these species has been detected during our work with this system. We have been using ethanol or methanol as solvent, instead of thf, and this is possibly the reason for the different reactivity observed. In fact, the role of the solvent in this sort of reaction is of prime importance, as has been observed for the system $NaBH_4$–$[FeCl_2(dmpe)_2]$ [dmpe = 1,2-bis(dimethylphosphino)ethane], which gives $[FeH(BH_4)(dmpe)_2]$ if the solvent is thf,[24] and $[FeH(H_2)(dmpe)_2]^+$ if the reaction is carried out in alcohols.[25] Furthermore, recent work on platinum hydride complexes has shown that $[\{Pt(dcpe)\}_2(\mu\text{-}H)_2]$ is readily protonated by water yielding $[Pt_2H_3(dcpe)_2]^+$.[26] This suggests that species such as $[\{Ni(L\text{–}L)\}_2(\mu\text{-}H)_2]$ (L–L = dippe or dcpe) may form initially in the reaction mixture, being readily protonated either by the alcohol used as solvent or by some water present, yielding the final trihydride species which are precipitated by addition of $Na[BPh_4]$. However, it has not been possible to deprotonate **2a** or **2b** using a strong base such as $KOBu^t$ in thf, and all attempts to prepare [{Ni(dippe)}$_2$(μ-H)$_2$] have so far been unsuccessful.

Experimental

All synthetic operations were routinely performed under a dry dinitrogen atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether and light petroleum (b.p. 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane[27] was prepared according to the literature. The IR spectra were recorded in Nujol mulls on a Perkin-Elmer 881 spectrophotometer, NMR spectra on Varian Unity 400 MHz or Varian Gemini 200 MHz spectrometers. Chemical shifts are given in ppm from SiMe$_4$ (^{1}H and ^{13}C-{^{1}H}) or 85% H$_3$PO$_4$ (^{31}P-{^{1}H}). The phosphine protons for all the compounds appeared in the correponding ^{1}H NMR spectra as a series of overlapping multiplets in the range δ 1–3, and were not assigned. Microanalyses were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

Preparations

[NiBr$_2$(dippe)] 1. To a mixture of anhydrous NiBr$_2$ (0.44 g, 2 mmol) in ethanol (30 cm^3) was added dippe (0.6 cm^3, *ca.* 2 mmol). An orange precipitate was formed immediately. The mixture was stirred for 30 min, or until all yellow NiBr$_2$ had disappeared. Then, the orange precipitate was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. This material can be used for synthetic purposes without any further purification. Analytically pure samples can be obtained by recrystallisation from dichloromethane or dichloromethane–ethanol. Yield: quantitative (Found: C, 35.0; H, 6.80. C$_{14}$H$_{32}$Br$_2$NiP$_2$ requires C, 34.95; H, 6.65%). NMR (CDCl$_3$): ^{31}P-{^{1}H}, δ 92.45 (s); ^{13}C-{^{1}H}, δ 18.71, 20.76 {s, P[CH(*C*H$_3$)$_2$]}, 22.71 (t, $|^1J_{CP} + {}^2J_{CP}| = 16$, PCH$_2$) and 27.68 {t, $|^1J_{CP} + {}^3J_{CP}| = 14$ Hz, P[*C*H(CH$_3$)$_2$]}.

[{Ni(dippe)}$_2$H$_3$][BPh$_4$] 2a. To a suspension of complex **1** (0.48 g, 1 mmol) in ethanol (20 cm^3) was added an excess of solid NaBH$_4$ (0.1 g). Gas evolution was observed. Upon stirring at room temperature for *ca.* 15 min a brown solution was obtained. Then an excess of Na[BPh$_4$] (0.5 g) dissolved in ethanol (10 cm^3) was added, and a golden-yellow precipitate was formed. This was filtered off, washed with EtOH and diethyl ether, and dried *in vacuo*. The crude product was extracted with several portions of hot acetone, and the solution filtered. Concentration and cooling to −20 °C afforded large red-orange crystals, which were filtered off, washed with light petroleum and dried *in vacuo*. Yield: quantitative (Found: C, 64.5; H, 9.30. C$_{52}$H$_{87}$BNi$_2$P$_4$ requires C, 64.7; H, 9.00%). IR: ν(NiH) 1673 cm^{-1}. NMR [(CD$_3$)$_2$CO]: ^{1}H, δ −13.357 (q, $^2J_{HP} = 26.6$); ^{31}P-{^{1}H}, δ 97.3 (s) (^{31}P selectively coupled to the hydride protons gave one quartet, $^2J_{HP} = 27$); ^{13}C-{^{1}H}, δ 19.14, 19.64 {s, P[CH(*C*H$_3$)$_2$]}, 22.58 (t, $|^1J_{CP} + {}^2J_{CP}| = 20.5$, PCH$_2$) and 25.98 {t, $|^1J_{CP} + {}^3J_{CP}| = 12.8$ Hz, P[*C*H(CH$_3$)$_2$]}.

[{Ni(dcpe)}$_2$H$_3$][BPh$_4$] 2b. This compound was obtained following a procedure analogous to that for **2a**, starting from [NiBr$_2$(dcpe)]. Yield: quantitative (Found: C, 70.8; H, 9.30. C$_{76}$H$_{119}$BNi$_2$P$_4$ requires C, 71.1; H, 9.25%). IR: ν(NiH) 1654 cm^{-1}. NMR [(CD$_3$)$_2$CO]: ^{1}H, δ −13.380 (q, $^2J_{HP} = 26.3$); ^{31}P-{^{1}H}, δ 87.09 (s); ^{13}C-{^{1}H}, δ 26.33, 26.74, 27.01 {s, P[CH(*C*H$_2$)$_5$]}, 27.23, 27.63 {t, $J_{CP} = 5.5$, P[CH(*C*H$_2$)$_5$]}, 25.67 (t, $|^1J_{CP} + {}^2J_{CP}| = 19.6$, PCH$_2$) and 35.08 {m, $|^1J_{CP} + {}^3J_{CP}| = 12$ Hz, P[*C*H(CH$_2$)$_5$]}.

Crystallography

A summary of crystallographic data for compound **2a** is given in Table 2. X-Ray measurements were made at 290 K on a crystal of dimensions 0.20 × 0.13 × 0.32 mm, mounted on a glass fibre and transferred to an AFC6S-Rigaku automatic diffractometer, using Mo-Kα graphite-monochromated radiation (λ 0.710 69 Å). Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the ω–2θ scan method. Lorentz polarisation, and absorption (ψ-scan method) corrections were applied. The transmission factors ranged from 0.95 to 1.00. The intensities of three standard reflections were monitored. A decay correction of 8.40% was applied. 4122 Reflections were collected, 3980 being unique ($R_{int} = 0.142$) and 1234 having $I > 3\sigma(I)$ were used for structure resolution. All calculations for data reduction,

Table 2 Summary of data for the crystal structure analysis of complex **2a**

Formula	C$_{52}$H$_{87}$BNi$_2$P$_4$
M	964.36
Crystal system	Monoclinic
Space group	*C*2/*c* (no. 15)
a/Å	18.153(8)
b/Å	33.515(6)
c/Å	11.635(5)
β/°	123.42(3)
U/Å^3	5908(8)
Z	4
D_c/g cm^{-3}	1.084
μ(Mo-Kα)/cm^{-1}	7.75
F(000)	2080
Scan speed (ω)/° min^{-1}	16
2θ Interval/°	5–45
Reflections collected	4122
Unique reflections	3980
Observed reflections ($I > 3\sigma_I$)	1234
Parameters	267
R^a	0.063
R' ($w = \sigma_F^{-2}$)^b	0.076
Goodness of fit	1.85

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

Table 3 Atomic fractional coordinates for [{Ni(dippe)}$_2$H$_3$][BPh$_4$]

Atom	*x*	*y*	*z*
Ni	0.430 4(2)	0.375 13(8)	0.231 3(2)
P(1)	0.381 7(3)	0.348 2(1)	0.344 7(4)
P(2)	0.304 7(3)	0.402 3(1)	0.094 3(5)
C(12)	0.263(1)	0.357 6(5)	0.253(2)
C(21)	0.237(1)	0.395 2(6)	0.166(2)
C(31)	0.411(1)	0.128 8(7)	0.640(2)
C(32)	0.395(2)	0.089 3(7)	0.669(2)
C(33)	0.321(2)	0.070 8(9)	0.579(3)
C(34)	0.258(2)	0.084(1)	0.461(4)
C(35)	0.266(1)	0.124(1)	0.424(2)
C(36)	0.344(1)	0.145 3(6)	0.513(2)
C(41)	0.530(1)	0.183 1(6)	0.666(2)
C(42)	0.519(1)	0.169 9(6)	0.544(2)
C(43)	0.552(2)	0.192 5(9)	0.479(2)
C(44)	0.593(2)	0.228 0(9)	0.530(3)
C(45)	0.608(1)	0.240 9(6)	0.650(3)
C(46)	0.579(1)	0.218 8(6)	0.721(2)
C(100)	0.393(1)	0.294 6(5)	0.376(2)
C(101)	0.365(1)	0.271 9(6)	0.243(2)
C(102)	0.346(2)	0.278 7(6)	0.444(2)
C(110)	0.433(1)	0.369 2(6)	0.518(2)
C(111)	0.527(2)	0.355 0(7)	0.616(2)
C(112)	0.430(1)	0.414 8(7)	0.514(2)
C(200)	0.240(1)	0.381 6(7)	−0.087(2)
C(201)	0.248(1)	0.335 7(7)	−0.076(2)
C(202)	0.147(2)	0.396 9(8)	−0.175(2)
C(220)	0.299(1)	0.456 6(5)	0.064(2)
C(221)	0.353(2)	0.478 8(6)	0.202(2)
C(222)	0.334(2)	0.465 8(6)	−0.031(3)
B	0.5	0.156(1)	0.75
H(1)	0.459(8)	0.352(4)	0.22(2)
H(2)	0.5	0.410(5)	0.25

structure solution, and refinement on F were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[28] software system and ORTEP[19] for plotting. The structure was solved by the Patterson method, and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. The hydride ligands H(1) and H(2) were located in regular Fourier-difference maps, and their positions allowed to refine with fixed isotropic thermal parameters. All other hydrogen atoms were included at idealised positions and not refined. Maximum and minimum peaks in the final Fourier-difference maps were $+0.36$ and -0.33 e Å ^{3}. Atomic coordinates are listed in Table 3.

Complete atomic coordinates, thermal perameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

Financial support from the Ministerio de Educación y Ciencia of Spain (Direccion General de Investigacion Científica y Técnica, Project PB91-0741, Programa Sectorial de Promoción General del Conocimiento) is gratefully acknowledged.

References

1 M. L. H. Green, C. N. Street and G. Wilkinson, *Z. Naturforsch., Teil B*, 1959, **14**, 738.
2 M. L. H. Green, T. Saito and J. Tanfield, *J. Chem. Soc. A*, 1971, 152.
3 K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 519.
4 T. Saito, *Chem. Lett.*, 1974, 1545.
5 H. C. Clark and A. Shower, *Can. J. Chem.*, 1975, **53**, 3462.
6 C. A. Ghilardi, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1975, **14**, 1790; L. Sacconi, A. Orlandini and S. Midollini, *Inorg. Chem.*, 1974, **13**, 2850.
7 K. Fisher, K. Jonas, P. Misbach, R. Stabba and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 943.
8 K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 312.
9 B. L. Barnett, C. Krüger, Y. H. Tsay, R. H. Summerville and R. Hoffman, *Chem. Ber.*, 1977, **110**, 3900.
10 K. R. Pörschke, W. Kleinmann, G. Wilke, K. H. Claus and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 991.
11 G. Longoni, M. Manassero and M. Sansoni, *J. Organomet. Chem.*, 1979, **174**, C41.
12 J. J. Schneider, R. Goddard, C. Krüger, S. Werner and B. Metz, *Chem. Ber.*, 1991, **124**, 1267.
13 G. Huttner and H. Lorentz, *Chem. Ber.*, 1974, **107**, 996.
14 T. F. Koetzle, J. Müller, D. L. Tipton, D. W. Hart and R. Bau, *J. Am. Chem. Soc.*, 1979, **101**, 5631.
15 A. S. Antsyshkyna, M. A. Porai-Koshits, V. N. Ostrikova, A. A. Pasynskii, Yu. V. Skripin and V. T. Kalinnikov, *Koord. Khim.*, 1982, **8**, 1552.
16 K. R. Pörschke, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1288.
17 O. Boutry, M. C. Nicasio, M. Paneque, E. Carmona, E. Gutierrez and C. Ruíz, *J. Organomet. Chem.*, 1993, **444**, 245.
18 E. Carmona, E. Gutierrez Puebla, J. M. Marín, A. Monge, M. Paneque, M. L. Poveda and C. Ruíz, *J. Am. Chem. Soc.*, 1989, **111**, 2883.
19 C. K. Johnson, ORTEP, A Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
20 R. A. Jones and B. R. Whittlesey, *Inorg. Chem.*, 1986, **25**, 852.
21 R. A. Jones, A. L. Stuart, J. L. Atwood, W. E. Hunter and R. D. Rogers, *Organometallics*, 1982, **1**, 1721.
22 (*a*) T. H. Tulip, T. Yamagata, T. Yoshida, R. D. Wilson, J. A. Ibers and S. Otsuka, *Inorg. Chem.*, 1978, **18**, 2239; (*b*) C. B. Knobler, H. D. Kaesz, G. Minghetti, A. L. Bandini, G. Banditelli and F. Bonati, *Inorg. Chem.*, 1983, **22**, 2324; (*c*) M. I. Chiang, R. Bau, G. Minghetti, A. L. Bandini, G. Banditelli and T. F. Koetzle, *Inorg. Chem.*, 1984, **23**, 124; (*d*) F. Bachechi, G. Bracher, D. M. Grove, B. Kellenberger, P. S. Pregosin, L. M. Venanzi and L. Zambonelli, *Inorg. Chem.*, 1983, **22**, 1031; (*e*) R. S. Paonessa and W. C. Trogler, *Inorg. Chem.*, 1983, **22**, 1038.
23 M. D. Fryzuk, J. B. Ng, S. J. Rettig, J. C. Huffman and K. Jonas, *Inorg. Chem.*, 1991, **30**, 2437.
24 M. V. Baker and L. D. Field, *J. Chem. Soc., Chem. Commun.*, 1984, 996.
25 M. V. Baker, L. D. Field and D. J. Young, *J. Chem. Soc., Chem. Commun.*, 1988, 546; A. Hills, D. L. Hughes, M. Jiménez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, 3041.
26 D. J. Schwartz and R. A. Andersen, *J. Am. Chem. Soc.*, 1995, **117**, 4014.
27 M. D. Fryzuk, T. Jones and F. W. B. Einstein, *Organometallics*, 1984, **3**, 185; T. A. Burt, J. Chatt, W. Hussain and G. J. Leigh, *J. Organomet. Chem.*, 1979, **182**, 237.
28 TEXSAN, Single-crystal Structure Analysis Software, version 5.0, Molecular Structure Corporation, Houston, TX, 1989.

Received 6*th October* 1995; *Paper* 5/06601H