Synthesis of cationic arene complexes of iron and ruthenium with 1,2-bis(diisopropylphosphino)ethane (dippe): X-ray crystal structures of [RuCl(η^6-C$_6$H$_6$)(dippe)][BPh$_4$] and [RuH(η^6-C$_6$H$_6$)(dippe)][BPh$_4$]

Isaac de los Ríos, Manuel Jiménez Tenorio, Miguel A. Jiménez Tenorio, M. Carmen Puerta *, Pedro Valerga

Dept. de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Aptdo. 40, 11510 Puerto Real, Cádiz, Spain

Abstract

The complex [FeCl$_2$(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with cyclohexadienyl-lithium in tetrahydrofuran yielding a dark mixture, from which the hydrido-arene complex [FeH(C$_6$H$_6$)(dippe)][BPh$_4$] (1) can be isolated in moderate yields upon treatment with MeOH–NaBPh$_4$. 1, as well as the toluene complex [FeH(C$_6$H$_5$Me)(dippe)][BPh$_4$] (2), can be prepared by reaction of [FeCl$_2$(dippe)] with Li^{n}Bu in benzene or toluene respectively, followed by MeOH–NaBPh$_4$. The ruthenium complexes [RuCl(L)(dippe)]$^+$ (L = C$_6$H$_6$, p-isopropylmethylbenzene (p-cymene)) are obtained by reaction of [{Ru(L)Cl$_2$}$_2$] with dippe and Ag$^+$, and isolated as the tetraphenylborate salts 3. These compounds react with NaBH$_4$ in acetone–ethanol furnishing the hydrido-arene derivatives [RuH(L)(dippe)][BPh$_4$] (L = C$_6$H$_6$ 5, p-cymene 6). All the compounds were characterized by IR, NMR and microanalysis. The X-ray crystal structures of 3 and 4 are also reported.

1. Introduction

Recently we reported the preparation of half-sandwich iron complexes of the type [Fe(L)Cl(dippe)] (L = C$_5$H$_5$, C$_5$Me$_5$; dippe = 1,2-bis(diisopropylphosphino)ethane), by reaction of [FeCl$_2$(dippe)] with either LiC$_5$H$_5$ or LiC$_5$Me$_5$ in tetrahydrofuran (thf) [1]. We found that these half-sandwich iron complexes are suitable precursors for paramagnetic 16-electron species [Fe(L)(dippe)]$^+$ (L = C$_5$H$_5$, C$_5$Me$_5$), which are reactive towards H$_2$ and N$_2$ [2]. The fact that the pentadienyl ligand may also stabilize paramagnetic, coordinatively unsaturated iron(II) complexes, such as [Fe(η^5-pentadienyl)(PEt$_3$)$_2$]$^+$ [3], prompted us to carry out the preparation of the related η^5-cyclohexadienyl iron derivatives, in order to compare their reactivities. However, attempts to prepare such complexes did not yield the expected results, despite the fact that compounds such as [FeH(η^5-C$_6$H$_7$)(dippe)] [4] and [FeH(η^5-

C$_6$H$_5$Me$_2$)(dippe)] [5] are known. The only product isolated from the reaction between [FeCl$_2$(dippe)] with cyclohexadienyl-lithium in thf, followed by NaBPh$_4$–MeOH, was the hydrido-arene complex [FeH(η^6-C$_6$H$_6$)(dippe)][BPh$_4$], in which aromatization of cyclohexadiene to benzene has taken place. Arene complexes of general formula [Fe(arene)L$_2$], such as [Fe(C$_6$H$_6$)-(η^2-C$_2$H$_4$)$_2$], [Fe(C$_6$H$_6$)(bipy)], or [Fe(C$_6$H$_6$)(PMe$_3$)$_2$], have mostly been prepared by metal-atom vapour synthesis methods [6]. More recently, a series of compounds of the type [Fe(arene)(dippe)] (arene = C$_6$H$_6$, C$_6$H$_5$Me, or C$_6$H$_4$Me$_2$) has been prepared by hydrogenation or thermolysis of high-spin iron(II) alkyls [5]. As far as we are aware, the only previously known hydrido-arene complexes of iron are of the type [FeH$_2$(arene)(SiCl$_3$)$_2$] (arene = C$_6$H$_6$, C$_6$H$_5$Me, or C$_6$H$_4$Me$_2$), and they were also prepared using metal vapour synthesis [7]. In contrast with this, arene complexes of ruthenium are far more common and stable. One possible reason for this may be the fact that the use of the readily available complexes [{Ru(arene)Cl$_2$}$_2$] [8] as starting materials allows an easy entry into the chemistry of these compounds. In this sense, arene
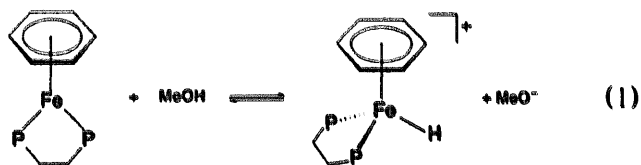
* Corresponding author.

complexes of ruthenium have attracted much attention not only because they represent one of the few examples of stable arene complexes amenable to isolation in high yield [9], but also because compounds such as [RuCl(arene)(BINAP)]$^+$ (arene = C_6H_6, cymene; X = Cl, Br, I; BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) may serve as excellent catalyst precursors for asymmetric hydrogenations [10]. In this work we report the synthesis and characterization of several cationic arene complexes of iron and ruthenium containing the bulky diphosphine dippe. The X-ray crystal structures of [RuX(C_6H_6)(dippe)][BPh$_4$] (X = Cl, H) are also described.

2. Results and discussion

The 14-electron complex [FeCl$_2$(dippe)] [11] reacts with cyclohexadienyl-lithium in thf at room temperature yielding a dark mixture, containing substantial amounts of metallic iron. Centrifugation, removal of the solvent and treatment of the residue with NaBPh$_4$–MeOH afforded a yellow, crystalline precipitate in about 25–30% yield. The yield does not improve when the reaction is carried out at −79°C. The ^{1}H NMR spectrum of this material displays one triplet at −14.194 ppm having a rather large coupling constant $^2J_{HP} = 81.6$ Hz, attributable to one hydridic proton coupled to two equivalent phosphorus atoms. No signals due to a coordinate cyclohexadienyl ligand were observed. Instead, one singlet at 5.960 ppm, characteristic for an η^6-C_6H_6 ligand, was present. The ^{31}P{^{1}H} NMR spectrum consists of one singlet, which splits to doublet when the spectrum is recorded in the proton-coupled mode. These spectral data, together with microanalysis, suggest that the product of this reaction is the hydrido-arene complex [FeH(η^6-C_6H_6)(dippe)][BPh$_4$] (1), although no ν(FeH) stretching band is observed in the IR spectrum of this compound. Thus, it seems that in the course of this reaction, aromatization of the cyclohexadienyl ring takes place, furnishing an η^6-C_6H_6 complex as final product. The Fe–H bond is stable, and spontaneous hydride migration to the benzene ring to yield coordinatively unsaturated [Fe(η^5-C_6H_7)(dippe)]$^+$, formally analogous to [Fe(η^5-C_5H_5)(dippe)]$^+$ [2], does not occur. Complex 1 is also obtained by reaction of [FeCl$_2$(dippe)] with Li^{n}Bu in benzene, followed by treatment with NaBPh$_4$–MeOH. If the reaction is carried out using toluene as solvent, then the ultimate product is the η^6-toluene derivative [FeH(C_6H_4Me)(dippe)][BPh$_4$] (2). This product has spectral properties which match those of compound 1, including the triplet for the hydride ligand at −14.631 ppm, with a $^2J_{HP} = 50$ Hz. The protons of the coordinated toluene ring appear as broadened singlets at 5.100 and 5.296 ppm, the latter being more intense, suggesting that it corresponds to two overlapping signals, as expected. The resonance of

the methyl group of the toluene appears as a singlet at 2.284 ppm. The ^{31}P{^{1}H} NMR spectrum also displays one singlet. The spectral data for both 1 and 2 are consistent with a 'three-legged' piano stool structure, similar to that found for half-sandwich iron and ruthenium complexes containing C_5H_5 or C_5Me_5, but having η^6-C_6H_6 or η^6-C_6H_5Me ligands instead. Despite the fact that crystals of these compounds were easily obtained, none of them was suitable for X-ray structure analysis. Attempts to prepare hydrido-arene derivatives containing η^6-C_6H_4Me$_2$ or η^6-C_6F_6 were unsuccessful. Very recently, the preparation has been reported of iron(0) arene complexes with dippe, from the hydrogenation or thermolysis of high-spin iron(II) alkyls. Thus, hydrogenation of the p-methylbenzyl complex [Fe(CH$_2$C$_6$H$_4$Me)$_2$(dippe)] gives several products, one of them being the iron(0) η^6-p-xylene complex [Fe(η^6-C_6H_4Me$_2$)(dippe)]. Other derivatives of the type [Fe(L)(dippe)] (L = η^6-C_6H_6, η^6-C_6H_4Me) have been prepared by reaction of [FeBr$_2$(dippe)] with MgEt$_2$ or Mg^{i}Bu$_2$ in an arene solvent [5]. In order to explain the formation of these compounds, it has been proposed that the dialkyls [FeR$_2$(dippe)] (R = Et or ^{i}Bu) are generated during the reaction, and their decomposition yields the highly reactive fragment {Fe(dippe)}, which is trapped by the arene solvent. Something similar may apply to our case, in which Li^{n}Bu reduces [FeCl$_2$(dippe)] to 'Fe(dippe)', and subsequently the corresponding iron(0) arene complex is generated in situ. Treatment of these arene complexes with MeOH affords the cationic hydrido-arene derivatives by protonation at the metal by the alcohol, according to the equilibrium

$$(1)$$

Addition of NaBPh$_4$ shifts the equilibrium to the right by precipitation of the corresponding salt [FeH(L)(dippe)][BPh$_4$] (L = C_6H_6 1 or C_6H_5Me 2). We have found no evidence in the literature referring to the protonation of compounds of the type [Fe(arene)L$_2$]. However, it has been observed that the ruthenium(0) complex [Ru(η^6-C_6H_6)(dcpe)] is protonated by p-nitrobenzyl alcohol under the conditions of a mass spectrometry experiment yielding the hydrido-arene cation [RuH(C_6H_6)(dcpe)]$^+$, which seems to be remarkably stable [9]. Attempts to deprotonate 1 or 2 using a strong base such as KO^{i}Bu were unsuccessful. The formation of 1 from cyclohexadienyl-lithium may follow a different reaction pathway since no aromatic solvent is present. The cyclohexadienyl complex [FeCl(η^5-C_6H_7)(dippe)] is possibly formed first. In MeOH, the chloride ligand eventually dissociates in a

fashion similar to what happens to [FeCl(C$_5$H$_5$)(dippe)] and [FeCl(C$_5$Me$_5$)(dippe)] [2], furnishing the 16-electron complex [Fe(η^5-C$_6$H$_7$)(dippe)]$^+$. This unstable cation undergoes a ring-metal hydrogen migration to give the more stable 18-electron cation [FeH(C$_6$H$_6$)(dippe)]$^+$, as shown in Eq. (2).

$$(2)$$
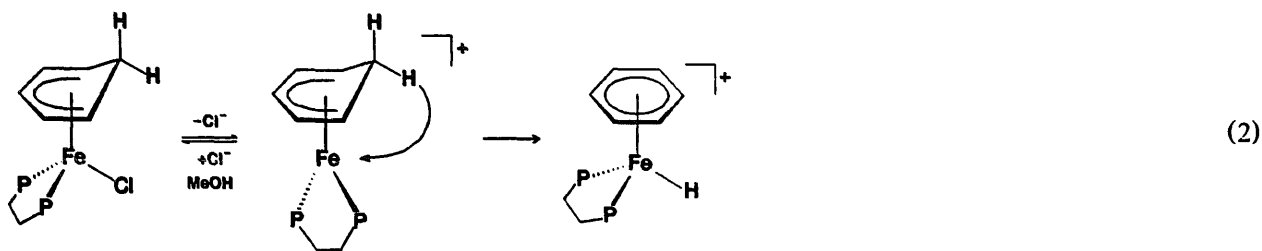
The driving force for such rearrangement should be not only the formation of a strong Fe–H bond, but also the aromatization of the cyclohexadienyl ring to benzene. Furthermore, the metal-promoted aromatization of cyclic 1,3- and 1,4-dienes is a well known process, which has been widely used for the preparation of arene complexes of ruthenium and osmium [8–12].

We have also prepared hydrido-arene derivatives of ruthenium, although following a different synthetic procedure. First, we prepared the chloro-complexes [RuCl(C$_6$H$_6$)(dippe)][BPh$_4$] (3) and [RuCl(cymene)(dippe)][BPh$_4$] (4) by reaction of the corresponding dimer [{Ru(L)Cl$_2$}$_2$}] (L = C$_6$H$_6$ or cymene) with dippe and CF$_3$SO$_3$Ag, which acts as chloride scavenger. This method is identical to that used recently for the preparation of [RuCl(C$_6$H$_6$)(dcpe)][CF$_3$SO$_3$] [9]. In some other instances the addition of a silver salt has been found to be unnecessary, i.e. in the preparation of [RuCl(arene)-(py)$_2$]$^+$ [11]. The resulting trifluoromethanesulphonate salts are then converted into the corresponding tetraphenylborate ones, by treatment with NaBPh$_4$=EtOH. The complexes 3 and 4 are yellow, crystalline, air-stable materials. The pattern displayed in the ^{1}H NMR spectrum of 3 is very similar to that of 1, except for the absence of the hydride signal. The benzene resonance appears as one singlet at 6.295 ppm, whereas the ^{1}H NMR spectrum of 4 is more complicated, due to the presence of the less symmetrical p-cymene ligand. The ring protons appear as two doublets at 5.676 and 5.568 ppm, with $^3J_{HH}$ = 6.4 Hz. The ring methyl substituent appears as one singlet at 1.443 ppm, whereas two resonances are observed for the isopropyl group as expected, one doublet and one septet. This pattern is characteristic of the η^6-cymene ligand, and matches the data in the literature for related complexes [8,10,12]. The ^{31}P{^{1}H} NMR spectra of 3 and 4 display one sharp singlet. These spectral data are consistent with a 'three-legged' piano stool geometry for the complex cations, as was proposed for the iron hydrido-arene derivatives 1 and 2. This has been demonstrated by an X-ray crystal structure analysis of compound 3. An ORTEP view of the complex cation [RuCl(C$_6$H$_6$)(dippe)]$^+$ is shown in

Fig. 1. Fractional atomic coordinates and B_{eq}, and selected bond lengths and angles are listed in Tables 1 and 2 respectively. Each unit cell contains two asymmetric units. The ruthenium atom is in a formally six-coordinate environment, and the cation has a 'three-legged' piano stool geometry. The Ru–Cl bond distance is very similar to that found in the related complexes [RuCl(C$_6$H$_5$Me)(dppb)][PF$_6$] (2.399 Å; dppb = 1,4-bis(diphenylphosphino)butane) [13], and in [RuCl(C$_6$H$_6$)(BINAP)][BF$_4$] (2.392 Å) [10], the Ru–P separations also being similar. All these parameters also compare well with those recently found for the pentamethylcyclopentadienyl derivative [RuCl(C$_5$Me$_5$)(dippe)] [14]. The C$_6$-ring of the benzene ligand in 3 is almost perfectly planar, with an average deviation of 0.021 Å from the plane. The Ru atom is at 1.752 Å from the plane, which forms a dihedral angle of 61° with the plane defined by the atoms Ru–P1–P2.

Both 3 and 4 react with an excess of NaBH$_4$ in acetone–ethanol furnishing the corresponding hydrido-arenes [RuH(C$_6$H$_6$)(dippe)][BPh$_4$] (5) and [RuH(cymene)(dippe)][BPh$_4$] (6), by metathetical exchange of chloride by hydride. This procedure has been previously
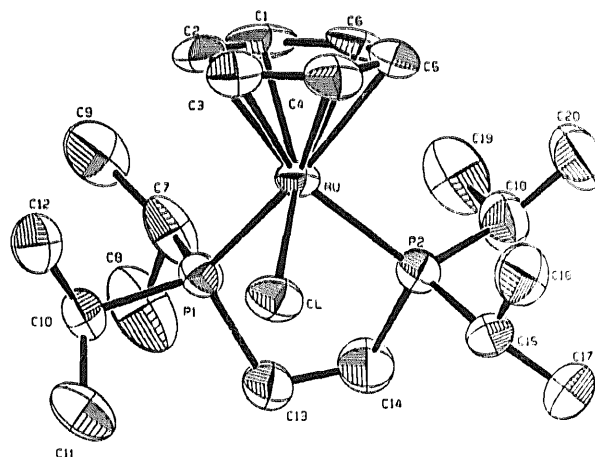

Fig. 1. ORTEP drawing of the complex cation [RuCl(C$_6$H$_6$)(dippe)]$^+$ with 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

Table 1
Atomic fractional coordinates and B_{eq} for [RuCl(C$_6$H$_6$)(dippe)][BPh$_4$]

Atom	x	y	z	B_{eq}
Ru	0.32301(4)	0.16392(5)	0.16836(3)	2.72(2)
Cl	0.3870(1)	0.2175(2)	0.2726(1)	4.2(1)
P(1)	0.2893(1)	0.3393(2)	0.1557(1)	3.25(8)
P(2)	0.1862(1)	0.1578(2)	0.2148(1)	3.7(1)
C(1)	0.3360(8)	0.1241(7)	0.0646(4)	5.2(5)
C(2)	0.4214(6)	0.1503(7)	0.0898(4)	4.8(5)
C(3)	0.4573(6)	0.1032(7)	0.1445(4)	4.4(4)
C(4)	0.4088(6)	0.0237(6)	0.1737(4)	4.2(4)
C(5)	0.3285(6)	−0.0079(6)	0.1478(4)	3.9(4)
C(6)	0.2880(6)	0.0448(7)	0.0944(4)	4.6(4)
C(7)	0.2350(6)	0.3781(6)	0.0765(5)	5.1(5)
C(8)	0.1828(7)	0.4792(8)	0.0806(6)	7.9(6)
C(9)	0.2978(8)	0.3825(7)	0.0220(4)	7.4(6)
C(10)	0.3757(5)	0.4382(6)	0.1681(4)	3.9(4)
C(11)	0.3803(6)	0.4884(7)	0.2342(5)	5.9(5)
C(12)	0.4653(6)	0.4033(7)	0.1489(5)	5.5(5)
C(13)	0.2115(6)	0.3681(7)	0.2195(4)	5.0(5)
C(14)	0.1412(6)	0.2893(7)	0.2199(5)	6.0(5)
C(15)	0.1918(6)	0.1112(7)	0.3009(4)	4.9(5)
C(16)	0.2455(7)	0.0146(8)	0.3121(4)	6.0(5)
C(17)	0.1018(8)	0.1031(8)	0.3299(5)	7.7(6)
C(18)	0.0912(6)	0.0912(7)	0.1733(5)	5.4(5)
C(19)	0.0717(6)	0.1289(8)	0.1043(6)	7.2(6)
C(20)	0.0943(7)	−0.0262(8)	0.1757(5)	7.1(6)
C(21)	−0.2562(5)	0.2041(6)	0.1571(4)	3.3(4)
C(22)	−0.3301(5)	0.2446(6)	0.1837(4)	3.6(4)
C(23)	−0.3361(6)	0.2583(6)	0.2505(5)	4.7(5)
C(24)	−0.2656(8)	0.2302(7)	0.2923(4)	5.6(5)
C(25)	−0.1919(7)	0.1920(7)	0.2691(4)	4.9(5)
C(26)	−0.1878(5)	0.1777(6)	0.2022(4)	4.2(4)
C(27)	−0.3347(5)	0.2122(6)	0.0331(4)	3.8(4)
C(28)	−0.3595(6)	0.3161(6)	0.0267(4)	4.8(5)
C(29)	−0.428(6)	0.3498(8)	−0.0157(5)	5.9(5)
C(30)	−0.4752(7)	0.281(1)	−0.0539(4)	6.2(6)
C(31)	−0.4545(6)	0.180(1)	−0.0492(4)	5.7(5)
C(32)	−0.3869(5)	0.1467(6)	−0.0059(4)	4.2(4)
C(33)	−0.2298(5)	0.0531(6)	0.0761(3)	3.1(3)
C(34)	−0.1525(5)	0.0082(6)	0.0587(4)	3.9(4)
C(35)	−0.1364(6)	−0.0971(8)	0.0624(4)	5.0(5)
C(36)	−0.1997(8)	−0.1592(8)	0.0831(4)	5.8(5)
C(37)	−0.2778(8)	−0.1204(8)	0.1017(4)	5.6(5)
C(38)	−0.2925(5)	−0.0148(7)	0.0985(4)	4.4(4)
C(39)	−0.1659(5)	0.2428(6)	0.0487(4)	3.3(4)
C(40)	−0.1424(6)	0.2267(6)	−0.0162(4)	4.3(4)
C(41)	−0.0734(6)	0.2766(8)	−0.0430(4)	5.1(5)
C(42)	−0.0247(5)	0.3489(7)	−0.0068(5)	4.7(5)
C(43)	−0.0476(6)	0.3693(6)	0.0560(5)	4.5(4)
C(44)	−0.1151(5)	0.3176(6)	0.0825(4)	3.7(4)
B	−0.2477(5)	0.1784(7)	0.0784(4)	3.3(4)

Table 2
Selected bond distances (Å) and angles (deg) for [RuCl(C$_6$H$_6$)(dippe)][BPh$_4$]

Intramolecular distances

Ru–Cl	2.398(2)	Ru–C(3)	2.261(8)
Ru–P(1)	2.346(2)	Ru–C(4)	2.237(7)
Ru–P(2)	2.328(2)	Ru–C(5)	2.273(8)
Ru–C(1)	2.204(7)	Ru–C(6)	2.208(7)
Ru–C(2)	2.257(8)		

Intramolecular angles

Cl–Ru–P(1)	83.82(7)	P(1)–Ru–C(3)	120.6(2)
Cl–Ru–P(2)	88.52(8)	P(1)–Ru–C(4)	156.7(3)
Cl–Ru–C(1)	150.7(3)	P(1)–Ru–C(5)	160.5(2)
Cl–Ru–C(2)	113.8(3)	P(1)–Ru–C(6)	124.1(2)
Cl–Ru–C(3)	88.0(2)	P(2)–Ru–C(1)	120.8(3)
Cl–Ru–C(4)	89.2(2)	P(2)–Ru–C(2)	157.6(3)
Cl–Ru–C(5)	115.6(2)	P(2)–Ru–C(3)	155.2(3)
Cl–Ru–C(6)	152.1(2)	P(2)–Ru–C(4)	118.7(2)
P(1)–Ru–P(2)	83.39(8)	P(2)–Ru–C(5)	94.8(2)
P(1)–Ru–C(1)	98.7(2)	P(2)–Ru–C(6)	93.9(3)
P(1)–Ru–C(2)	98.4(2)		

triplet attributable to the hydride ligand coupled to two equivalent phosphorus atoms. This signal appears at slightly lower field than in the iron complexes 1 or 2. Apart from this signal, the rest of the spectrum is very similar to that of the corresponding chloro-complexes 4 or 5. The ^{31}P{^{1}H} NMR spectra display one singlet in both cases, which again suggests a 'three-legged' piano stool structure for these derivatives. The X-ray crystal structure of 4 was determined. The structure of the cation [RuH(C$_6$H$_6$)(dippe)]$^+$ is represented in Fig. 2. Fractional atomic coordinates and B_{eq}, and selected bond lengths and angles are listed in Tables 3 and 4 respectively.

The structure of [RuH(C$_6$H$_6$)(dippe)]$^+$ is very similar to that of [RuCl(C$_6$H$_6$)(dippe)]$^+$. The hydride atom

used for the preparation of [RuH(C$_6$H$_6$)(depe)][CF$_3$SO$_3$] [9]. Attempts to replace chloride by an alkyl group using Grignard reagents were unsuccessful, the starting material being recovered from these reactions. The ruthenium hydrido-arene derivatives are white (5) or brown (6) crystalline materials, which exhibit one medium ν(RuH) band near 2054 cm^{-1} in their IR spectra. The ^{1}H NMR spectra display one high-field
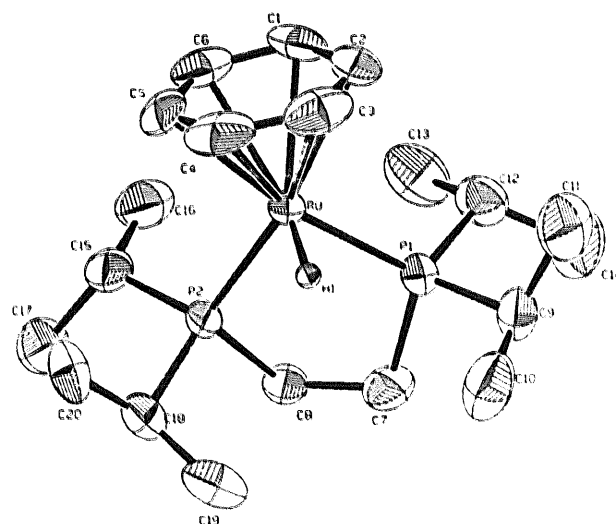

Fig. 2. ORTEP drawing of the complex cation [RuH(C$_6$H$_6$)(dippe)]$^+$ with 50% probability thermal ellipsoids. Hydrogen atoms, except hydride, are omitted.

was located on the final regular difference Fourier map and refined with fixed isotropic thermal parameters. It appears at 1.32(8) Å from the Ru atom, a distance which is very short for a Ru–H bond, if we compare it with the values found for the related compound [RuH(C_6H_5Me)(PPh$_3$)$_2$][BPh$_4$] (1.635 Å) [15]. However, an Ru–H separation of 1.36(8) Å has been reported for [RuH(C_5H_5)(PMe$_3$)$_2$] [16], a value which is

Table 3

Atomic fractional coordinates and B_{eq} for [RuH(C_6H_6)(dippe)][BPh$_4$]

Atom	x	y	z	B_{eq}
Ru	0.37942(8)	0.05174(3)	0.22544(4)	2.52(3)
P(1)	0.4009(3)	−0.0000(1)	0.3324(2)	3.1(1)
P(2)	0.3550(3)	0.1300(1)	0.3011(1)	2.9(1)
C(1)	0.200(1)	0.0062(5)	0.1555(6)	4.2(6)
C(2)	0.325(1)	−0.0239(5)	0.1488(6)	4.4(6)
C(3)	0.444(1)	0.0041(6)	0.1259(6)	5.0(6)
C(4)	0.435(1)	0.0639(7)	0.1082(5)	5.3(7)
C(5)	0.313(1)	0.0938(5)	0.1154(5)	4.6(6)
C(6)	0.198(1)	0.0649(6)	0.1384(6)	4.3(6)
C(7)	0.422(1)	0.0486(5)	0.4129(5)	4.1(5)
C(8)	0.346(1)	0.1059(4)	0.3985(5)	3.6(5)
C(9)	0.555(1)	−0.0480(5)	0.3461(5)	4.0(5)
C(10)	0.691(1)	−0.0175(6)	0.3430(7)	6.2(7)
C(11)	0.546(1)	−0.0984(5)	0.2912(7)	6.6(7)
C(12)	0.256(1)	−0.0485(5)	0.3521(6)	4.4(5)
C(13)	0.119(1)	−0.0153(5)	0.3572(7)	5.9(7)
C(14)	0.282(1)	−0.0885(6)	0.4199(8)	7.8(8)
C(15)	0.197(1)	0.1733(5)	0.2825(5)	4.3(5)
C(16)	0.066(1)	0.1410(5)	0.2917(6)	4.9(6)
C(17)	0.194(1)	0.2306(5)	0.3258(7)	6.1(7)
C(18)	0.496(1)	0.1844(4)	0.3069(6)	4.1(6)
C(19)	0.634(1)	0.1602(5)	0.3401(7)	5.5(7)
C(20)	0.513(1)	0.2098(5)	0.2291(7)	6.3(7)
C(21)	0.8412(9)	0.1248(4)	1.0468(5)	2.4(4)
C(22)	0.814(1)	0.1284(4)	1.1221(5)	3.0(5)
C(23)	0.805(1)	0.0803(5)	1.1679(6)	4.0(5)
C(24)	0.826(1)	0.0253(5)	1.1406(6)	4.3(6)
C(25)	0.850(1)	0.0197(4)	1.0664(6)	3.8(5)
C(26)	0.856(1)	0.0682(4)	1.0214(5)	3.5(5)
C(27)	0.884(1)	0.1681(4)	0.9115(5)	2.8(5)
C(28)	1.013(1)	0.1424(4)	0.9037(6)	3.5(5)
C(29)	1.062(1)	0.1302(5)	0.8352(8)	5.1(7)
C(30)	0.985(2)	0.1444(5)	0.7716(7)	5.5(7)
C(31)	0.860(1)	0.1700(5)	0.7758(6)	4.8(6)
C(32)	0.808(1)	0.1819(4)	0.8452(6)	3.7(5)
C(33)	0.937(1)	0.2351(4)	1.0260(5)	2.6(4)
C(34)	1.029(1)	0.2333(4)	1.0884(5)	3.3(5)
C(35)	1.115(1)	0.2790(5)	1.1109(6)	4.5(6)
C(36)	1.114(1)	0.3291(4)	1.0716(6)	3.9(5)
C(37)	1.024(1)	0.3333(4)	1.0085(6)	4.1(6)
C(38)	0.939(1)	0.2880(5)	0.9873(5)	3.8(5)
C(39)	0.672(1)	0.2023(4)	0.9923(5)	2.5(4)
C(40)	0.567(1)	0.1674(4)	0.9592(6)	3.8(5)
C(41)	0.427(1)	0.1784(5)	0.9601(6)	4.5(6)
C(42)	0.383(1)	0.2267(6)	0.9973(6)	4.8(6)
C(43)	0.483(1)	0.2622(5)	1.0312(6)	4.7(6)
C(44)	0.623(1)	0.2502(5)	1.0283(6)	3.8(5)
B	0.834(1)	0.1828(5)	0.9940(6)	2.8(5)
H(1)	0.515(8)	0.054(3)	0.241(4)	3.0

Table 4

Selected bond distances (Å) and angles (deg) for [RuH(C_6H_6)(dippe)][BPh$_4$]

Intramolecular distances

Ru–P(1)	2.266(3)	Ru–C(4)	2.24(1)
Ru–P(2)	2.280(3)	Ru–C(5)	2.26(1)
Ru–C(1)	2.32(1)	Ru–C(6)	2.29(1)
Ru–C(2)	2.26(1)	Ru–H(1)	1.32(8)
Ru–C(3)	2.23(1)		

Intramolecular angles

P(1)–Ru–P(2)	84.8(1)	P(2)–Ru–C(1)	125.3(3)
P(1)–Ru–C(1)	104.4(3)	P(2)–Ru–C(2)	160.7(3)
P(1)–Ru–C(2)	97.1(3)	P(2)–Ru–C(3)	156.4(4)
P(1)–Ru–C(3)	114.6(4)	P(2)–Ru–C(4)	120.7(4)
P(1)–Ru–C(4)	149.2(4)	P(2)–Ru–C(5)	98.9(3)
P(1)–Ru–C(5)	167.6(4)	P(2)–Ru–C(6)	101.6(3)
P(1)–Ru–C(6)	132.4(3)	P(2)–Ru–H(1)	89.0(30)
P(1)–Ru–H(1)	79.0(30)		

similar to ours. In any case, we must always consider that metal–hydrogen bond lengths determined by X-ray crystallography may be subject to considerable inaccuracy. The Ru–P separations in 5 are slightly shorter than in the chloro-complex 3, whereas the distance from the plane of the C_6H_6 ring (mean deviation from plane 0.004 Å) to ruthenium is longer (1.788 Å). The C_6H_6–RuP$_2$ interplanar angle has a value of 72.6°, which is more open than in compound 3, and reflects the smaller steric requirements of the hydride ligand compared with chloride. All other bond lengths and angles, including dippe and the [BPh$_4$]$^-$ anion, are in the range expected, being unexceptional.

3. Conclusions

The reaction of [FeCl$_2$(dippe)] with alkyl-lithium reagents in an aromatic solvent such as benzene or toluene, followed by treatment with Na[BPh$_4$]–MeOH has shown to be a useful synthetic route to the hydrido-arene derivatives [FeH(Ar)(dippe)][BPh$_4$] (Ar = C_6H_6, C_6H_5Me), a rather uncommon class of iron compounds. More common ruthenium complexes of the type [RuX(Ar)(dippe)][BPh$_4$] (Ar = C_6H_6, *p*-cymene; X = Cl, H) have been also prepared, and two of them structurally characterized, expanding in this way the range of known stable arene ruthenium derivatives.

4. Experimental section

All synthesis operations were performed under a dry dinitrogen atmosphere following conventional Schlenk techniques. Thf, diethyl ether and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated

immediately before use. 1,2-Bis(diisopropylphosphino)-ethane [17], [FeCl₂(dippe)] [11] and [{Ru(*p*-cymene)Cl₂}₂] [8] were prepared according to literature. [{Ru(C₆H₆)Cl₂}₂] was supplied by Aldrich. IR spectra were recorded in Nujol mulls on a Perkin–Elmer 881 spectrophotometer. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from SiMe₄ (^{1}H and ^{13}C{^{1}H}) or 85% H₃PO₄ (^{31}P{^{1}H}). The phosphine protons for all the compounds appeared in the corresponding ^{1}H NMR spectra as a series of overlapping multiplets in the range 1–3 ppm, and were not assigned. Microanalysis were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

4.1. [FeH(C₆H₆)(dippe)][BPh₄] (1)

To [FeCl₂(dippe)] (0.39 g, 1 mmol) in thf, a solution of cyclohexadiene in thf, prepared in situ from 1,4-cyclohexadiene (0.1 ml, ca. 1 mmol) and ^{n}BuLi (0.65 ml of a 1.6 M solution in hexanes, ca. 1 mmol) was added. A darkening of the solution was immediately observed. The mixture was stirred at room temperature for 10 min. Then, it was taken to dryness, the residue extracted with MeOH, and the resulting yellow-green solution filtered through Celite, in order to remove finely divided metallic iron. Addition of an excess of NaBPh₄ yielded a yellow-green precipitate, which was filtered, washed with petroleum ether and dried in vacuo. Recrystallization from acetone–ethanol at −20°C afforded yellow needles of the pure compound. Yield: 0.2 g, 28%. Anal. Found: C, 73.8; H, 8.35. C₄₄H₅₉BFeP₂ requires C, 73.8; H, 8.24%. NMR (CD₃COCD₃): ^{1}H δ 5.960 (s, C₆H₆); −14.194 (t, $^2J_{HP}$ = 81.6 Hz, Fe*H*). ^{31}P{^{1}H} 117.8 s. ^{13}C{^{1}H} 18.24, 18.36, 19.01, 19.84 (s, P(CH(CH₃)₂)); 21.12 (t, J_{CP} = 19.3 Hz, PCH₂); signals for P(C*H*(CH₃)₂) obscured by solvent peaks; 89.39 (s, C₆H₆).

4.2. [FeH(C₆H₅Me)(dippe)][BPh₄] (2)

To a solution of [FeCl₂(dippe)] (0.6 g, ca. 1.5 mmol) in toluene, Li^{n}Bu (2.1 ml of a 1.6 M solution in hexanes, ca. 3.4 mmol) was added. A dark mixture was immediately obtained, which was stirred at room temperature for 30 min. Then, the solvent was removed in vacuo. The residue was extracted with MeOH, and the solution filtered through Celite or centrifuged. Addition of an excess of Na[BPh₄] to this solution yielded a yellow precipitate, which was filtered, washed with ethanol and petroleum ether, and dried in vacuo. Recrystallization from acetone–ethanol or thf–ethanol afforded yellow needles of compound 2. Yield: 0.35 g, 32%. Anal. Found: C, 73.8; H, 8.30. C₄₅H₆₁BFeP₂ requires C, 74.0; H, 8.36%. NMR (CDCl₃): ^{1}H δ 5.296, 5.100 (s, br, C₆H₅CH₃); 2.284 (s, C₆H₅C*H*₃);

−14.631 (t, $^2J_{HP}$ = 50 Hz, Fe*H*). ^{31}P{^{1}H} 114.95 s. ^{13}C{^{1}H} 17.92, 17.99, 18.72, 19.44 (s, P(CH(CH₃)₂)); 20.56 (t, J_{CP} = 19.0 Hz, PCH₂); 28.08 (t, J_{CP} = 13.5 Hz, P(*C*H(CH₃)₂)), 28.20 (m, P(*C*H(CH₃)₂)); 21.82 (s, CH₃C₆H₅); 84.62, 88.42, 90.12 (s, CH₃C₆H₅). This procedure can also be used for the preparation of compound 1, using benzene as solvent instead of toluene.

4.3. [RuCl(C₆H₆)(dippe)][BPh₄] (3)

To [{Ru(C₆H₆)Cl₂}₂] (0.5 g, 1 mmol) in thf, dippe (0.6 ml, ca. 2 mmol) and CF₃SO₃Ag (0.5 g, 2 mmol) was added. An orange solution and a precipitate of AgCl were formed. The mixture was refluxed for 2 h. Then, the solvent was removed in vacuo. The residue was extracted with ethanol, and the resulting solution centrifuged. Concentration and cooling to −20°C at this stage, allows the isolation of the trifluoromethyl-sulphonate salt [RuCl(C₆H₆)(dippe)][CF₃SO₃] as yellow-orange crystals, if desired. Addition of an excess of solid Na[BPh₄] to the solution yielded a yellow-orange precipitate of 3, which was filtered, washed with ethanol and petroleum ether, and dried in vacuo. Recrystallization from acetone–ethanol afforded orange crystals. Yield: 1.3 g, 83%. Anal. Found: C, 66.3; H, 7.35. C₄₄H₅₈BClP₂Ru requires C, 66.4; H, 7.29%. NMR (CDCl₃): ^{1}H δ 6.295 (s, C₆H₆). ^{31}P{^{1}H} 83.87 s. ^{13}C{^{1}H} 19.49, 19.64, 19.97 (s, P(CH(CH₃)₂)); 21.16 (t, J_{CP} = 19.1 Hz, PCH₂); 26.59 (t, J_{CP} = 13.9 Hz, P(*C*H(CH₃)₂)), 31.13 (t, J_{CP} = 11.4 Hz, P(*C*H(CH₃)₂)); 91.91 (t, J_{CP} = 2.57 Hz, C₆H₆).

4.4. [RuCl(cymene)(dippe)][BPh₄] (4)

This compound was obtained in a fashion analogous to that for 3, starting from [{Ru(cymene)Cl₂}₂], and the appropriate amounts of dippe and AgCF₃SO₃ in thf. Yield: 65%. Anal. Found: C, 67.8; H, 7.84. C₄₈H₆₆BClP₂Ru requires C, 67.6; H, 7.75%. NMR (CDCl₃): ^{1}H δ 5.676, 5.568 (d, J_{HH} = 6.4 Hz, CH₃C₆H₄CH(CH₃)₂), 2.561 (sept, J_{HH} = 6.8 Hz, CH₃C₆H₄C*H*(CH₃)₂), 1.443 (s, C*H*₃C₆H₄CH(CH₃)₂), 1.227 (d, J_{HH} = 6.8 Hz, CH₃C₆H₄CH(C*H*₃)₂). ^{31}P{^{1}H} 81.01 s. ^{13}C{^{1}H} 19.20, 19.30, 19.53, 19.82 (s, P(CH(CH₃)₂)); 20.30 (t, J_{CP} = 19.1 Hz, PCH₂); 25.88 (t, J_{CP} = 13.8 Hz, P(*C*H(CH₃)₂)), 29.15 (t, J_{CP} = 11. Hz, P(*C*H(CH₃)₂)); 94.04, 92.04 (s, CH₃C₆H₄CH(CH₃)₂), 87.09 (t, J_{CP} = 4.2 Hz, CH₃C₆H₄CH(CH₃)₂); 30.72 (s, CH₃C₆H₄CH(CH₃)₂); 21.56 (s, CH₃C₆H₄CH(C*H*₃)₂); 17.52 (s, CH₃C₆H₄CH(CH₃)₂).

4.5. [RuH(C₆H₆)(dippe)][BPh₄] (5)

To a solution of compound 3 (0.4 g, 0.5 mmol) in acetone, an excess of NaBH₄ was added. The mixture

was stirred for 30 min. Then, ethanol was added, and the solution was filtered through Celite. Concentration and cooling to $-20\,^\circ$C yielded colourless crystals of **5**, which were suitable for X-ray crystal structure analysis. Yield: 0.26 g, 68%. Anal. Found: C, 69.1; H, 7.56. $C_{44}H_{59}BP_2Ru$ requires C, 69.3; H, 7.75%. IR: ν(RuH) 2045 cm^{-1}. NMR (CDCl$_3$): ^{1}H δ 6.179 (s, C_6H_6); -12.056 (t, $^2J_{HP} = 35.4$ Hz, RuH). ^{31}P{^{1}H} 106.66 s. ^{13}C{^{1}H} 17.72, 18.06, 18.66, 19.51 (s, P(CH(CH_3)$_2$)); 20.65 (t, $J_{CP} = 20.2$ Hz, PCH_2); 27.01 (t, $J_{CP} = 16.5$ Hz, P(CH(CH$_3$)$_2$)), 28.62 (t, $J_{CP} = 11.8$ Hz, P(CH(CH$_3$)$_2$)); 90.46 (t, $J_{CP} = 1.7$ Hz, C_6H_6).

4.6. [RuH(cymene)(dippe)][BPh$_4$] (6)

This compound was obtained in the form of brown crystals, following a procedure identical to that outlined above for compound **5**, starting from [RuCl(cymene)(dippe)][BPh$_4$]. Yield: 75%. Anal. Found: C, 71.0; H, 7.92. $C_{48}H_{64}BP_2Ru$ requires C, 70.8; H, 7.86%. IR: ν(RuH) 2045 cm^{-1}. NMR (CDCl$_3$): ^{1}H δ 5.443, 5.342 (d, $J_{HH} = 6.8$ Hz, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$), 2.489 (sept, $J_{HH} = 6.8$ Hz, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$), 2.012 (s, CH_3C$_6$H$_4$CH(CH$_3$)$_2$), 1.295 (d, $J_{HH} = 6.8$ Hz,

CH$_3$C$_6$H$_4$CH(CH_3)$_2$); -12.823 (t, $^2J_{HP} = 36.6$ Hz, RuH). ^{31}P{^{1}H} 105.95 s. ^{13}C{^{1}H} 17.50, 17.85, 18.73, 19.17 (s, P(CH(CH_3)$_2$)); 20.52 (t, $J_{CP} = 19.9$ Hz, PCH_2); 26.94 (t, $J_{CP} = 16.8$ Hz, P(CH(CH$_3$)$_2$)), 28.20 (t, $J_{CP} = 11.1$ Hz, P(CH(CH$_3$)$_2$)); 106.51, 94.63, 82.69 (s, C H $_3C_6$H $_4$C H (C H $_3$)$_2$); 32.56 (s, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$); 24.20 (s, CH$_3$C$_6$H$_4$CH(CH_3)$_2$); 19.46 (s, CH_3C$_6$H$_4$CH(CH$_3$)$_2$).

4.7. Experimental data for the X-ray crystal structure determinations

A summary of crystallographic data for compounds **3** and **5** is given in Table 5. X-ray measurements were made on crystals of the appropriate size, which were mounted onto a glass fibre, and transferred to an AFC6S-Rigaku automatic diffractometer, using Mo Kα graphite-monochromated radiation. Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the ω–2θ scan method. Lorentz, polarization, and absorption (ψ-scan method) corrections were applied. Three standard reflections were intensity controlled, in order to establish a decay correction. Reflections having $I > 3\sigma(I)$ were used for struc-

Table 5
Summary of data for the crystal structure analysis of 3 and 5

Compound	3	5
Formula	$C_{44}H_{58}BClP_2Ru$	$C_{44}H_{59}BP_2Ru$
F.W.	796.22	761.78
Crystal size (mm^3)	$0.25 \times 0.13 \times 0.27$	$0.14 \times 0.16 \times 0.29$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Cell parameters		
a (Å)	15.162(4)	9.653(4)
b (Å)	12.985(3)	22.963(7)
c (Å)	20.454(5)	18.075(4)
β (deg)	93.03(2)	94.04(2)
Volume (Å^3)	4021(2)	3997(2)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.315	1.266
T (K)	290	290
λ(Mo Kα)(Å)	0.71069	0.71069
μ(Mo Kα)(cm^{-1})	5.56	4.91
$F(000)$	1672	1608
Absorption correction	ψ-method	ψ-method
Transmision factors	0.92–1.00	0.96–1.00
Scan speed (ω) (deg min^{-1})	8	4
2θ interval (deg)	$5 < 2\theta < 45$	$5 < 2\theta < 45$
Measured reflections	7775	7739
Unique reflections	7477 ($R_{int} = 0.141$)	7287 ($R_{int} = 0.234$)
Observed reflections ($I > 3\sigma_I$)	3433	3118
Number of parameters	442	436
Reflection/parameter ratio	7.77	7.15
R [a]	0.046	0.054
R_w ($w = \sigma F^{-2}$) [b]	0.053	0.063
Maximum Δ/σ in final cycle	0.39	0.26
G.o.f.	1.62	1.64

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

ture resolution. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN [18] software system and ORTEP [19] for plotting. Both structures were solved by the Patterson method, and anisotropically refined by full-matrix least squares methods for all non-hydrogen atoms. The hydride atom in **5** was located on a final difference Fourier map as the most intense peak, and it was allowed to refine with isotropic fixed thermal parameters. All other hydrogen atoms were included at idealised positions and not refined. Maximum and minimum peaks in the final difference Fourier maps were $+0.99$ and $-0.46\,e\,\text{Å}^{-3}$ for **3**, and $+0.98$ and $-0.55\,e\,\text{Å}^{-3}$ for **5**. Fractional atomic coordinates and B_{eq}, and selected bond lengths and angles for each compound are listed in Tables 2–5.

5. Supplementary material

Tables of X-ray crystallographic data, including atomic coordinates and anisotropic thermal parameters, interatomic distances and angles (44 pages), and listings of calculated and observed structure factors (25 pages) are available. Ordering information is given on any current masthead page.

Acknowledgements

References

[1] M. Jiménez Tenorio, M.C. Puerta and P. Valerga, *Organometallics*, *113* (1994) 3330.

[2] A. de la Jara Leal, M. Jiménez Tenorio, M.C. Puerta and P. Valerga, *Organometallics*, *114* (1995) 3839.

[3] J.R. Bleeke, R.J. Wittenbrink, T.W. Clayton, Jr. and H.Y. Chiang, *J. Am. Chem. Soc.*, *112* (1990) 6539.

[4] R. Benn, H. Brennecke, A. Frings, H. Lemhkuhl, G. Mehler, A. Rufinska and T. Wildt, *J. Am. Chem. Soc.*, *110* (1988) 5661.

[5] A.R. Hermes, T.H. Warren and G.S. Girolami, *J. Chem. Soc. Dalton Trans.*, (1995) 301.

[6] L.J. Radonovich, M.W. Eyring, T.J. Groshens and K.J. Klabunde, *J. Am. Chem. Soc.*, *104* (1982) 2816; U. Zenneck and W. Franck, *Angew. Chem. Int. Ed. Engl.*, *25* (1986) 831; M.L.H. Green and L.-L. Wong, *J. Chem. Soc. Dalton Trans.*, (1987) 411; S.D. Ittel, F.A. Van Catledge and J.P. Jesson, *J. Am. Chem. Soc.*, *101* (1979) 3874.

[7] Z. Yao, K.J. Klabunde and S. Asirvasthan, *Inorg. Chem.*, *34* (1995) 5289.

[8] M.A. Bennett and A.K. Smith, *J. Chem. Soc. Dalton Trans.*, (1974) 233.

[9] F.L. Joslin and D.M. Roundhill, *Organometallics*, *11* (1992) 1749.

[10] K. Mashima, K. Kusano, T. Ohta, R. Noyori and H. Takaya, *J. Chem. Soc. Chem. Commun.*, (1989) 1208.

[11] A.R. Hermes and G.S. Girolami, *Inorg. Chem.*, *27* (1988) 1775.

[12] T. Arthur and T.A. Stephenson, *J. Organomet. Chem.*, *208* (1981) 369.

[13] I.S. Thorburn, S.J. Rettig and B.R. James, *J. Organomet. Chem.*, *296* (1985) 103.

[14] I. de los Ríos, M. Jiménez Tenorio, J. Padilla, M.C. Puerta, and P. Valerga, *J. Chem. Soc. Dalton Trans.*, (1996) 377.

[15] A.R. Siedle, A.R. Newmark, L.H. Pignolet, D.X. Wang and T.A. Albright, *Organometallics*, *5* (1986) 38.

[16] F.R. Lemke and L. Brummer, *Organometallics*, *14* (1995) 3980.

[17] M.D. Fryzuk, T. Jones and F.W.B. Einstein, *Organometallics*, *3* (1984) 185; T.A. Burt, J. Chatt, W. Hussain and G.J. Leigh, *J. Organomet. Chem.*, *182* (1979) 237.

[18] TEXSAN, *Single-Crystal Structure Analysis Software*, version 5.0, Molecular Structure Corporation, Texas, 1989.

[19] C.K. Johnson, ORTEP, *A Thermal Ellipsoid Plotting Program*, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.