

Reactions of $[\text{Cp}^*\text{RuCl}(\text{PP})]$ ($\text{PP} = \text{dppm}, \text{dppe}$) with NaBAR'_4 : Structural Characterization of $\{[\text{Cp}^*\text{Ru}]_2(\mu\text{-Cl})(\mu\text{-dppm})_2\}[\text{BAR}'_4]$ and of $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dppm})][\text{BAR}'_4]$ ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$)

Halikhedkar Aneetha, Manuel Jiménez-Tenorio, M. Carmen Puerta, and Pedro Valerga*

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

Kurt Mereiter

Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

Received October 22, 2002

Summary: The reaction of $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ with NaBAR'_4 in fluorobenzene under argon generates the binuclear complex $\{[\text{Cp}^*\text{Ru}]_2(\mu\text{-Cl})(\mu\text{-dppm})_2\}[\text{BAR}'_4]$, which has been structurally characterized. No complex was isolated from the reaction of $[\text{Cp}^*\text{RuCl}(\text{dppe})]$ with NaBAR'_4 under argon, but halide abstraction from $[\text{Cp}^*\text{RuCl}(\text{PP})]$ ($\text{PP} = \text{dppm}, \text{dppe}$) under dinitrogen using NaBAR'_4 yielded the corresponding cationic terminal dinitrogen complexes $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{PP})][\text{BAR}'_4]$.

Introduction

The introduction of the noncoordinating anion $[\text{BAR}'_4]^-$ ($\text{BAR}'_4 = \text{tetrakis}(3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl})\text{borate}$) as halide scavenger has recently allowed the isolation of a series of coordinatively unsaturated cationic complexes of the type $[\text{Cp}^*\text{Ru}(\text{PP})][\text{BAR}'_4]$ ($\text{PP} = 1,2\text{-bis}(\text{diisopropylphosphino})\text{ethane}$ (dippe), $(\text{PMe}^i\text{Pr}_2)_2$, $(\text{PEt}_3)_2$, $(\text{PPh}^i\text{Pr}_2)_2$, $(\text{PPh}_3)_2$).¹ Whereas some of these compounds have been subjected to X-ray structure analysis, others decomposed readily to a variety of final products, most often to species containing $\eta^6\text{-arene}$ moieties. In an attempt to synthesize the Cp counterparts of these complexes, we carried out the reaction of $[\text{CpRuCl}(\text{PP})]$ ($\text{PP} = \text{dippe}$, $(\text{PMe}^i\text{Pr}_2)_2$, $(\text{PEt}_3)_2$) with NaBAR'_4 under Ar. However, in these cases, the 16-electron species were too reactive to be detected, as they react with traces of N_2 present in the argon, furnishing the dinitrogen-bridged complexes $\{[\text{CpRu}(\text{PP})]_2(\mu\text{-N}_2)\}[\text{BAR}'_4]_2$. Only the reaction of $[\text{CpRuCl}(\text{PMe}^i\text{Pr}_2)(\text{PPh}_3)]$ with NaBAR'_4 under Ar yielded a cationic compound of formula $[\text{CpRu}(\text{PMe}^i\text{Pr}_2)(\text{PPh}_3)][\text{BAR}'_4]$, which however turned out to be an 18-electron complex containing a rare $\eta^3\text{-PPh}_3$ ligand.² To finish the survey of the range of phosphine ligands capable of stabilizing cationic 16-electron species, we have now examined the reactivity of two well-

known systems, namely $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ and $[\text{Cp}^*\text{RuCl}(\text{dppe})]$, toward NaBAR'_4 in fluorobenzene both under argon and under dinitrogen. Despite the fact that the moieties $\{[\text{Cp}^*\text{Ru}(\text{dppm})]^+\}$ and $\{[\text{Cp}^*\text{Ru}(\text{dppe})]^+\}$ can be generated in situ and constitute binding sites for a range of small molecules such as dihydrogen,³ dioxygen,^{4,5} and dinitrogen,⁶ no cationic 16-electron species could be isolated. In this note we describe the outcome of these experiments, which complete our works on this subject.^{1,2}

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere by following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. Solvents were deoxygenated by three freeze/pump/thaw cycles and stored under argon. $\text{Na}[\text{BAR}'_4]$,⁷ $[\text{Cp}^*\text{RuCl}(\text{dppm})]$,⁸ and $[\text{Cp}^*\text{RuCl}(\text{dppe})]$ ^{4a} were prepared according to reported procedures. IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were obtained on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in parts per million from SiMe_4 (^1H) or 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$). Microanalysis was performed by the Serveis Científic-Tècnics, Universitat de Barcelona.

$\{[\text{Cp}^*\text{Ru}]_2(\mu\text{-Cl})(\mu\text{-dppm})_2\}[\text{BAR}'_4]$ (1). To a solution of $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ (0.33 g, 0.5 mmol) in fluorobenzene (15 mL) under argon was added solid NaBAR'_4 (0.44 g, 0.5 mmol). The mixture was stirred for 15 min at room temperature. The initial yellow-orange solution was converted to a red suspension. Sodium chloride was removed by filtration through Celite. The resulting solution was layered with petroleum ether and

* To whom correspondence should be addressed. E-mail: pedro.valerga@uca.es.

(1) (a) Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2000**, *122*, 11230. (b) Aneetha, H.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Sapunov, V. N.; Schmid, R.; Kirchner, K.; Mereiter, K. *Organometallics* **2002**, *21*, 5334.

(2) Aneetha, H.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Mereiter, K. *Organometallics* **2002**, *21*, 628.

(3) (a) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. (b) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677.

(4) (a) Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Inorg. Chim. Acta* **1995**, *236*, 95. (b) Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1993**, 892.

(5) Jia, G.; Ng, W. S.; Chu, H. S.; Wong, W.-T.; Yu, N.-T.; Williams, I. D. *Organometallics* **1999**, *18*, 3597.

(6) Hembre, R. T.; McQueen, S. *J. Am. Chem. Soc.* **1994**, *116*, 2141.

(7) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

(8) Lin, W.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1997**, *16*, 2987.

Table 1. Summary of Crystallographic Data for Compounds 1 and 2

	1·solv ^a	2
formula	C ₁₀₆ H ₈₆ BClF ₂₄ P ₄ Ru ₂	C ₆₇ H ₄₉ BF ₂₄ N ₂ P ₂ Ru
fw	2188.03	1511.90
T (K)	297(2)	223(2)
cryst size (mm)	0.40 × 0.22 × 0.18	0.75 × 0.65 × 0.50
cryst syst	monoclinic	triclinic
space group	P2 ₁ /n (No. 14)	P1̄ (No. 2)
cell params		
a (Å)	16.575(8)	12.579(3)
b (Å)	31.380(14)	14.410(3)
c (Å)	19.692(9)	20.033(3)
α (deg)		80.36(1)
β (deg)	90.61(1)	71.77(1)
γ (deg)		83.21(1)
V (Å ³)	10242(8)	3392(1)
Z	4	2
ρ _{calcd} (g cm ⁻³)	1.419	1.480
μ (Mo Kα) (cm ⁻¹)	4.73	3.86
F(000)	4432	1520
max. min transmissn factors	1.000, 0.897	1.000, 0.935
θ range for data collec (deg)	1.60–25.00	1.44–30.00
no. of rflns collected	103 542	60 455
no. of unique rflns	17 893 (R _{int} = 0.048)	19 292 (R _{int} = 0.019)
no. of obsd rflns (I > 2σ)	14 290	16 472
no. of params	1243	942
final R1, wR2 values (I > 2σ)	0.0535, 0.1350	0.0471, 0.1174
final R1, wR2 values (all data)	0.0710, 0.1535	0.0564, 0.1270
residual electron density peaks (e Å ⁻³)	+0.94, -0.71	+0.93, -0.51

^a Contains petroleum ether with four solvent peaks per asymmetric unit, which have been included as carbon atoms in chemical formula and derived quantities.

left standing undisturbed at room temperature. Well-formed red crystals were obtained by slow diffusion of the petroleum ether into the fluorobenzene solution. These crystals were isolated by cannulating off the supernatant liquor, washed with petroleum ether, and dried under an argon stream. Yield: 0.32 g, 60%. Anal. Calcd for C₁₀₂H₈₆BClF₂₄P₄Ru₂: C, 57.2; H, 4.02. Found: C, 57.5; H, 3.90. ¹H NMR (CD₂Cl₂): δ 1.25 s (C₅(CH₃)₅); 2.78, 2.82 (m, PCH₂); 6.80, 7.09, 7.19, 7.30, 7.47 (m, PC₆H₅). ³¹P{¹H} NMR (CD₂Cl₂): δ 39.04 s.

[Cp*₂Ru(N₂(dppm))][BAR'₄] (2). Yellow crystals of this compound were obtained in a fashion analogous to that for **1**, starting from [Cp*₂RuCl(dppm)] (0.33 g, 0.5 mmol) and NaBAR'₄ (0.44 g, 0.5 mmol) in fluorobenzene (15 mL), under a dinitrogen atmosphere instead of argon. Yield: 0.49 g, 66%. Anal. Calcd for C₆₇H₄₉BF₂₄N₂P₂Ru: C, 53.2; H, 3.24; N, 1.85. Found: C, 53.0; H, 3.12; N, 1.5. IR: ν(N₂) 2166 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 1.64 s (C₅(CH₃)₅); 4.58, 5.28 (m, PCH₂); 7.37, 7.44, 7.54 (m, PC₆H₅). ³¹P{¹H} NMR (CD₂Cl₂): δ 3.98 s.

[Cp*₂Ru(N₂(dppe))][BAR'₄] (3). This compound was obtained in a fashion analogous to that for **2**, starting from [Cp*₂RuCl(dppe)] (0.33 g, 0.5 mmol) and NaBAR'₄ (0.44 g, 0.5 mmol) in fluorobenzene (15 mL). Yield: 0.52 g, 68%. Anal. Calcd for C₆₉H₅₃BF₂₄N₂P₂Ru: C, 53.8; H, 3.44; N, 1.82. Found: C, 53.6; H, 3.40; N 1.5. IR: ν(N₂) 2159 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 1.52 s (C₅(CH₃)₅); 2.52, 2.64 (m, PCH₂); 6.98, 7.41, 7.59 (m, PC₆H₅). ³¹P{¹H} NMR (CD₂Cl₂): δ 71.8 s.

X-ray Structure Determinations. Crystals of **1** (in the form of **1**·solv) and **2** were obtained by slow diffusion of petroleum ether into fluorobenzene solutions at -20 °C. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, 0.3° ω-scan frames covering complete spheres of the reciprocal space). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were

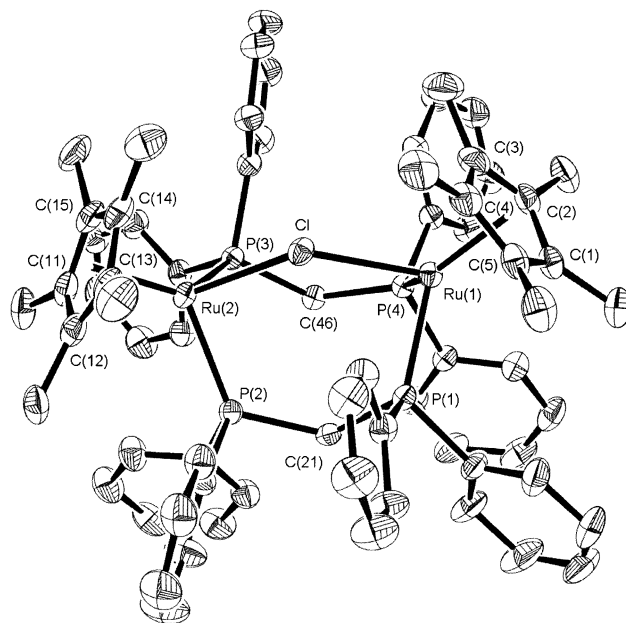


Figure 1. ORTEP drawing (30% thermal ellipsoids) of the cation $[\{Cp^*Ru\}_2(\mu-Cl)(\mu-dppm)_2]^+$ in complex **1**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru(1)–Cl = 2.466(1); Ru(1)–C(1) = 2.242(5); Ru(1)–C(2) = 2.275(5); Ru(1)–C(3) = 2.250(5); Ru(1)–C(4) = 2.248(5); Ru(1)–C(5) = 2.273(5); Ru(1)–P(1) = 2.319(1); Ru(1)–P(4) = 2.331(1); Ru(2)–Cl = 2.454(1); Ru(2)–C(11) = 2.226(5); Ru(2)–C(12) = 2.268(5); Ru(2)–C(13) = 2.263(5); Ru(2)–C(14) = 2.246(5); Ru(2)–C(15) = 2.255(5); Ru(2)–P(2) = 2.335(1); Ru(2)–P(3) = 2.325(1); Ru(1)–Cl–Ru(2) = 134.49(5); P(1)–Ru(1)–P(4) = 91.50(4); P(2)–Ru(2)–P(3) = 94.79(4); P(1)–C(21)–P(2) = 126.8(2); P(3)–C(46)–P(4) = 125.8(2).

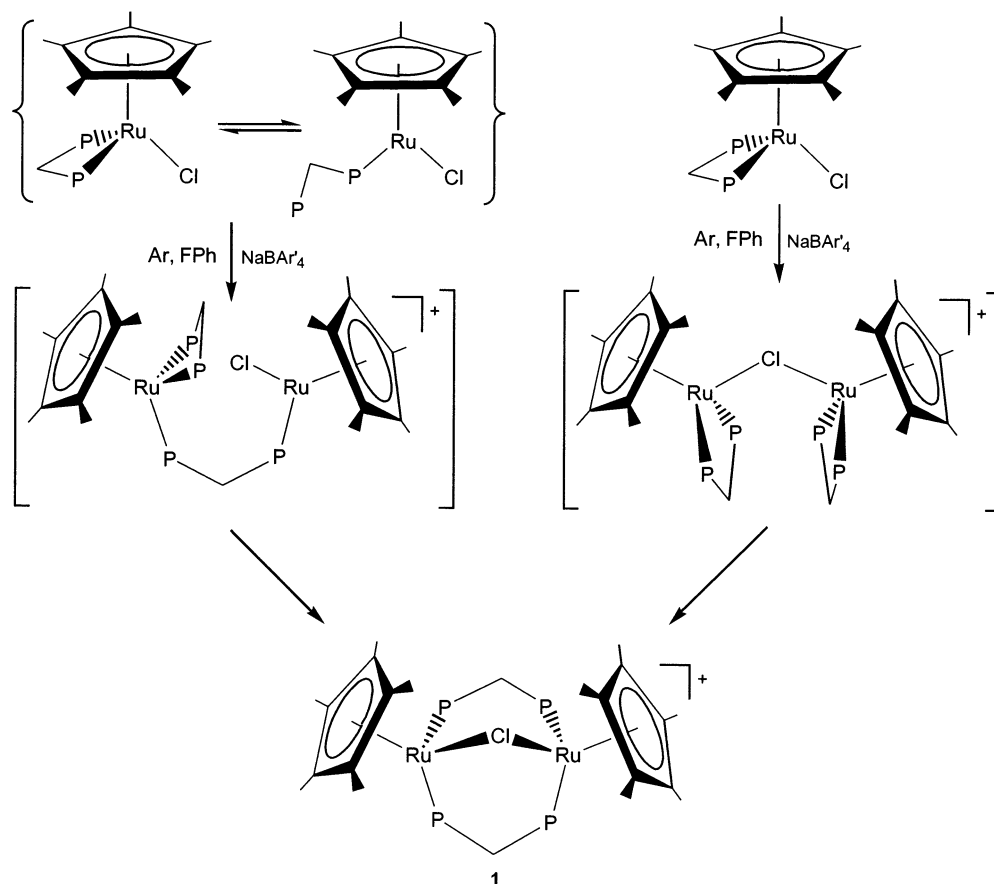
applied. All structures were solved by direct methods using the program SHELXS97.⁹ Structure refinement on F^2 was carried out with the program SHELXL97.⁹ ORTEP¹⁰ was used for plotting.

Results and Discussion

The reaction of [Cp*₂RuCl(dppm)][BAR'₄] with NaBAR'₄ in fluorobenzene under argon yielded a dark red solution, at variance with other [Cp*₂RuCl(PP)] (PP = dippe, (PEt₃)₂, (PPh₃)₂) complexes, for which deep blue solutions are generated under similar conditions.¹ The blue color in these systems is indicative of the generation of stable cationic 16-electron species, something that apparently does occur in the dppm system. Workup of the reaction mixture afforded red crystals which were subjected to X-ray structure analysis, turning out to be the dinuclear complex $[\{Cp^*Ru\}_2(\mu-Cl)(\mu-dppm)_2][BAR'_4]$ (**1**). Figure 1 shows an ORTEP view of the dinuclear complex cation. There are one chloride and two dppm ligands acting as bridges between the two ruthenium atoms. The Ru(1)–Ru(2) separation of 4.537(1) Å suggests that there is no metal–metal bonding interaction, at variance with the Ru^{III}–Ru^{III} dinuclear complex

(9) (a) SHELXS97, Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1997. (b) SHELXL97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(10) Johnson, C. K. ORTEP, A Thermal Ellipsoid Plotting Program; Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

Scheme 1. Proposed Reaction Sequence for the Formation of **1** at the Expense of $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ 

$[\{\text{Cp}^*\text{Ru}\}_2(\mu\text{-Cl})_2(\mu\text{-dppm})][\text{CF}_3\text{SO}_3]_2$, which contains one Ru–Ru bond with a separation of 2.921(1) Å.¹¹ The bond lengths and angles of the bridging chloride and dppm ligands compare well with data in the literature for other dppm-bridged Cp^*Ru complexes. It is not clear how the dinuclear complex cation **1** is generated. Its formation could be easily explained if we assume that the starting material $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ had a dimeric nature, i.e., $[\{\text{Cp}^*\text{RuCl}\}_2(\mu\text{-dppm})_2]$, as has been found for the related complex $[\{\text{Cp}^*\text{RuCl}\}_2(\mu\text{-dmpm})_2]$ (dmpm = $\text{Me}_2\text{PCH}_2\text{PMe}_2$).⁸ It has been found that the standard procedure for the preparation of $[\text{Cp}^*\text{RuCl}(\text{PP})]$ complexes, namely the addition of phosphine to $[\{\text{Cp}^*\text{RuCl}\}_4]$ in a suitable solvent, yields in the case of dppm the dinuclear species $[\{\text{Cp}^*\text{Ru}\}_2(\mu\text{-Cl})_2(\mu\text{-dppm})]$ irrespective of the phosphine-to-metal ratio, if the solvent is Et_2O or THF,⁸ or even CH_2Cl_2 if the dppm is added over a 2 h period in order to minimize the formation of monomeric $[\text{Cp}^*\text{RuCl}(\text{dppm})]$.¹¹ Girolami and co-workers have shown that pure $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ can be obtained using MeCN as solvent, presumably due to the intermediacy of $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$.⁸ In our case, we checked carefully by NMR the starting material to ensure that it was monomeric $[\text{Cp}^*\text{RuCl}(\text{dppm})]$. Therefore, **1** is actually formed at the expense of $[\text{Cp}^*\text{RuCl}(\text{dppm})]$. We can tentatively postulate the reaction sequence shown in Scheme 1 to account for the formation of **1**. Given the strong tendency of dppm to adopt η^1 or a bridging coordination mode,^{8,11,12} a fast ring-opening equilibrium

between the chelate $[\text{Cp}^*\text{RuCl}(\eta^2\text{-dppm})]$ and the pendant-arm 16-electron species $[\text{Cp}^*\text{RuCl}(\eta^1\text{-dppm})]$ should be possible. The reaction of the latter with $[\text{Cp}^*\text{Ru}(\text{dppm})]^+$ generated in situ upon chloride abstraction would yield the dppm-bridged species $[\{\text{Cp}^*\text{Ru}(\text{dppm})\}_2(\mu\text{-dppm})\{\text{Cp}^*\text{RuCl}\}]^+$. A rearrangement within this species would lead to **1**. In a variant of this reaction sequence, once the chloride is removed, the resulting 16-electron cation might react with the chloride ligand of $[\text{Cp}^*\text{RuCl}(\text{dppm})]$, giving $[\{\text{Cp}^*\text{Ru}(\text{dppm})\}_2(\mu\text{-Cl})]^+$ as intermediate, which upon rearrangement would yield **1**. As has been mentioned, these are just tentative proposals. Other alternative explanations cannot be disregarded. No pure product was obtained from the reaction of $[\text{Cp}^*\text{RuCl}(\text{dppe})]$ with NaBAR_4 in fluorobenzene under argon. When the reagents were mixed, the mixture took on a brown color, with no trace of blue or red. Workup of the reaction mixture only yielded dark brown oily substances, which were not characterized.

The reaction of both $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ and $[\text{Cp}^*\text{RuCl}(\text{dppe})]$ with NaBAR_4 under dinitrogen is more straightforward and leads to the corresponding terminal dinitrogen complexes $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dppm})][\text{BAR}'_4]$ (**2**) and $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dppe})][\text{BAR}'_4]$ (**3**). These compounds are yellow materials, which exhibit one strong $\nu(\text{N}_2)$ band in their IR spectra at 2166 cm^{-1} for **2** and 2159 cm^{-1} for **3**. These compounds add to the series of end-on and bridging half-sandwich ruthenium dinitrogen complexes

(11) Mauthner, K.; Kalt, D.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **1997**, *128*, 533.

(12) Orth, S. D.; Terry, M. R.; Abboud, K. A.; Dodson, B.; McElwee-White, L. *Inorg. Chem.* **1996**, *35*, 916. Kölle, U.; Hörnig, A.; Englert, U. *J. Organomet. Chem.* **1992**, *438*, 309. Albers, M. O.; Liles, D. C.; Robinson, D. J.; Singleton, E. *Organometallics* **1987**, *6*, 2179.

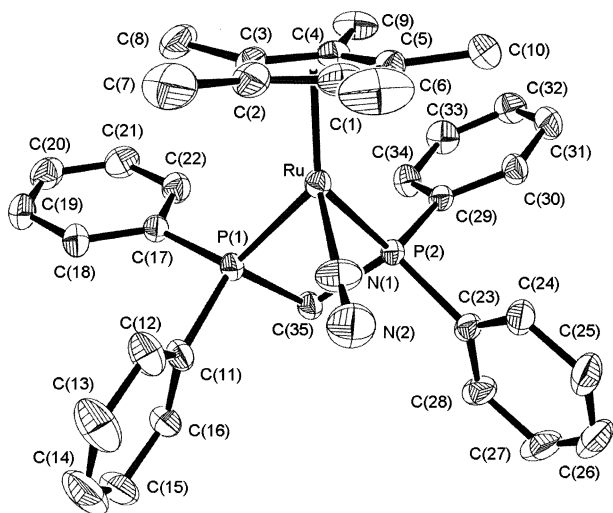


Figure 2. ORTEP drawing (30% thermal ellipsoids) of the cation $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dppm})]^+$ in complex **2**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru–N(1) = 1.975(2); Ru–C(1) = 2.239(3); Ru–C(2) = 2.224(3); Ru–C(3) = 2.244(2); Ru–C(4) = 2.233(2); Ru–C(5) = 2.235(2); Ru–P(1) = 2.3311(7); Ru–P(2) = 2.3309(6); N(1)–N(2) = 1.083(4); Ru–N(1)–N(2) = 175.7(3); P(1)–Ru–P(2) = 71.44(2); P(1)–C(35)–P(2) = 94.7(1).

already reported by our research group.^{2,13} It must be mentioned that $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dppm})]^+$ was detected in the course of the reaction of the monohydride $[\text{Cp}^*\text{RuH}(\text{dppm})]$ with the hydride acceptor *N*-methylacridinium hexafluorophosphate under dinitrogen, in an attempt to model the reactivity of the hydrogenase enzyme with the dihydrogen complex $[\text{Cp}^*\text{Ru}(\text{H}_2)(\text{dppm})]^+$.⁶ The value of 2169 cm^{-1} reported for $\nu(\text{N}_2)$ in $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dppm})][\text{PF}_6]$ ⁶ is consistent with ours for **2**. However, Jia and co-workers did not observe $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dppm})]^+$ in their studies of the interaction of $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ with aerial oxygen.⁵ The X-ray crystal structure of **2** has been determined. An ORTEP view of the dinitrogen complex cation is shown in Figure 2. The cation has a typical three-legged piano-stool structure, with the dinitrogen ligand bound in an end-on manner, with a Ru–N(1)–N(2) angle of 175.7(3)°. The N(1)–N(2) bond distance of 1.083(4) Å is essentially identical with that of the free

dinitrogen molecule, whereas the Ru–N(1) separation of 1.975(2) Å compares well with the value of 1.961(3) Å found in $[\text{Cp}\text{Ru}(\text{N}_2)(\text{dippe})][\text{BAR}'_4]$,² being in the range observed for other terminal Ru–N₂ complexes.¹⁴ The reason the bond distance in the dinitrogen molecule in these complexes does not change to a great extent upon coordination to a metal center has been interpreted elsewhere in terms of EHMO calculations.^{14b}

Summing up, halide abstraction from either $[\text{Cp}^*\text{RuCl}(\text{dppm})]$ or $[\text{Cp}^*\text{RuCl}(\text{dippe})]$ using NaBAR'_4 under argon does not lead to isolable cationic 16-electron compounds, whereas both systems are capable of stabilizing the Ru–N₂ bond. From a total of 10 different phosphine ligands studied in systems of the types $[\text{Cp}^*\text{RuCl}(\text{PP})]$ (PP = dippe, $(\text{PET}_3)_2$, $(\text{PPh}_3)_2$, $(\text{PMe}_3)_2$, dppe, dppm) and $[\text{Cp}^*\text{RuCl}(\text{P}) + \text{P}$ (P = PMe^iPr_2 , PPh^iPr_2 , P^iPr_3 , PCy_3), only in five cases were cationic 16-electron $[\text{Cp}^*\text{Ru}(\text{PP})]^+$ detected, and in three cases they were crystallized.¹ No genuine 16-electron species were isolated or detected using Cp instead of Cp* as coligand.² Several monodentate phosphine ligands which keep a fine balance between donor abilities and steric hindrance are capable of stabilizing cationic half-sandwich 16-electron species. However, this is only accomplished in the case of bidentate phosphine ligands by using the bulky, strongly electron releasing phosphine dippe. It remains to be seen whether bulkier bidentate ligands of the type $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ (R = ^tBu, Cy, *n* = 2, 3) can effectively contribute to the stabilization of such unsaturated complexes.

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología (DGICYT, Project BQU2001-4046) and the Ministerio de Asuntos Exteriores of Spain (Accion Integrada HU2001-0020) for financial support and Johnson Matthey plc for generous loans of ruthenium trichloride.

Supporting Information Available: Tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020880L

(13) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2000**, 609, 161. de los Ríos, I.; Jiménez-Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1996**, 15, 4565.

(14) (a) Jiménez-Tenorio, M. A.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1998**, 3601. (b) Gemel, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1996**, 4071. (c) Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1997**, 16, 1253. (d) Jia, G.; Meek, D. W.; Gallucci, J. C. *Inorg. Chem.* **1991**, 30, 403.