Bridging and Terminal Half-Sandwich Ruthenium Dinitrogen Complexes and Related Derivatives: A Structural Study

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The reaction of [CpRuCl(P)$_2$] [(P)$_2$ = dippe (1,2-bis(diisopropylphosphino)ethane; (PEt$_3$)$_2$; (PMe^{i}Pr$_2$)$_2$] with Na[BAr′$_4$] (Ar′$_4$ = 3,5-bis(trifluoromethyl)phenyl) in fluorobenzene under argon generates the corresponding cationic 16-electron species [CpRu(P)$_2$]$^+$, which reacts with trace amounts of dinitrogen present even in high-purity argon furnishing the dinitrogen-bridged complexes [{CpRu(P)$_2$}$_2$(μ-N$_2$)][BAr′$_4$]$_2$ [(P)$_2$ = dippe **1a**; (PEt$_3$)$_2$ **1b**; (PMe^{i}Pr$_2$)$_2$ **1c**]. If the reaction is performed under dinitrogen, the terminal dinitrogen complexes [CpRu(N$_2$)(P)$_2$][BAr′$_4$] [(P)$_2$ = dippe **2a**; (PMe^{i}Pr$_2$)$_2$ **2c**] are obtained. Compound **1b** was obtained irrespectively of the atmosphere used, and no terminal dinitrogen complex has been detected. The crystal structures of **1a**, **1b**, and **2a** have been determined. During one attempt to isolate the 16-electron complex [CpRu(PMe^{i}Pr$_2$)$_2$][BAr′$_4$], the 18-electron tris(phosphine) derivative [CpRu(PMe^{i}Pr$_2$)$_3$][BAr′$_4$], **3**, was obtained instead, and it was structurally characterized. Halide abstraction from [CpRuCl(PMe^{i}Pr$_2$)(PPh$_3$)] under dinitrogen using Na[BAr′$_4$] yielded [CpRu(N$_2$)(PMe^{i}Pr$_2$)(PPh$_3$)][BAr′$_4$], **2d**, but under argon the complex [CpRu(PMe^{i}Pr$_2$)(PPh$_3$)][BAr′$_4$], **4**, which contains a rare η^3-coordinated PPh$_3$ ligand as shown by X-ray crystallography, was isolated.

Introduction

Cationic 16-electron species of the type [(C$_5$R$_5$)Ru(P)$_2$]$^+$ (R = H, Me) have been postulated as intermediates in many reactions involving the well-known half-sandwich halo complexes [(C$_5$R$_5$)RuX(P)$_2$].[1] These coordinatively unsaturated species can be generated by halide abstraction from the latter by using a suitable halide scavenger reagent, most often Ag$^+$ or Tl$^+$ salts. However, the [(C$_5$R$_5$)Ru(P)$_2$]$^+$ cations generated in situ are extremely reactive species, which usually react with any suitable donor molecule in the reaction mixture, furnishing 18-electron complexes. The donor can be a solvent molecule, particularly if it is coordinating, i.e., MeCN, acetone, THF, etc. The counterion may also act as a ligand. Even poorly coordinating anions such as [CF$_3$SO$_3$]$^-$, [BF$_4$]$^-$, or even [BPh$_4$]$^-$ are known to bind to a metal center. Thus, reports claiming the isolation of 16-electron complexes such as [CpRu(dcpe)][CF$_3$SO$_3$] (dcpe = 1,2-bis(dicyclohexylphosphino)ethane)[2] or [Cp*Ru(dppe)][CF$_3$SO$_3$] (dppe = 1,2-bis(diphenylphosphino)ethane)[3] might actually correspond to the 18-electron derivatives[CpRu(CF$_3$SO$_3$)(dcpe)] or [Cp*Ru(CF$_3$SO$_3$)(dppe)], respectively. Under these conditions, we have shown that dinitrogen becomes a good ligand, furnishing half-sandwich ruthenium dinitrogen complexes of the type [(C$_5$R$_5$)Ru(N$_2$)(P)$_2$]$^+$ [R = H or Me, (P)$_2$ = 1,2-bis(diisopropylphosphino)ethane (dippe); R = Me, (P)$_2$ = (PEt$_3$)$_2$].[4,5] At variance with their hydrotris(pyrazolyl)borate counterparts [TpRu(N$_2$)(P)$_2$]$^+$ [(P)$_2$ = dippe; (PEt$_3$)$_2$],[6,7] the complexes [(C$_5$R$_5$)Ru(N$_2$)(P)$_2$]$^+$ are extremely labile, and all attempts to purify these materials by recrystallization led to dinitrogen loss and formation of different species ranging from dioxygen complexes [Cp*Ru(O$_2$)(P$_2$)]$^{+8}$ to the sandwich derivative [CpRu(η^6-C$_6$H$_5$BPh$_3$)].[4] The introduction of the bulky, noncoordinating anion [BAr′$_4$]$^{-\ 9}$ and its use as halide scavenger in combination with fluorobenzene as solvent opens new possibilities for the generation and stabiliza-

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tion of highly electrophilic cationic complexes. Thus, following the recent isolation of remarkably stable coordinatively unsaturated complexes [(C_5R_5)Ru(N−N)][BAr′$_4$] (R = Me, N−N = $Me_2NCH_2CH_2NMe_2$, $Me_2NCH_2CH_2N^iBu_2$; R = H, N−N = $Me_2NCH_2CH_2NMe_2$),[10,11] we have been able to synthesize the first genuine cationic 16-electron half-sandwich ruthenium phosphine complexes [Cp*Ru(P)$_2$][BAr′$_4$] [(P)$_2$ = dippe, $(PMe^iPr_2)_2$].[12] These compounds are extremely reactive deep blue materials, which have been unequivocally characterized by X-ray structure analysis. We have now carried out the halide abstraction reactions from a series of cyclopentadienyl phosphine complexes [CpRuCl(P)$_2$] using Na[BAr′$_4$] in fluorobenzene, with the aim of isolating the corresponding 16-electron complexes [CpRu(P)$_2$][BAr′$_4$]. Indeed, these species are generated, but they have shown to have an enormous avidity for dinitrogen. Hence, they react even with trace amounts of N_2 present in high-purity argon, furnishing the dinitrogen-bridged complexes [{CpRu(P)$_2$}$_2$(μ-N_2)][BAr′$_4$]$_2$ [(P)$_2$ = dippe **1a**; $(PEt_3)_2$ **1b**; $(PMe^iPr_2)_2$ **1c**]. Only when aromatic substituents were present on one of the phosphine ligands was a compound of formula [CpRu(PPh_3)(PMe^iPr_2)][BAr′$_4$] isolated, but it turned out to be an 18-electron species, in which one C=C bond from one of the aromatic rings fills the vacant coordination site, leading to a rare η^3-coordination mode for the PPh_3 ligand. The synthesis, structure, and spectral properties of all these compounds and of related species are described in detail in the present work.

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. [CpRuCl(dippe)],[8] [CpRuCl(PEt_3)$_2$],[13] and [CpRuCl(PMe^iPr_2)(PPh_3)][13] were prepared according to reported procedures. A new, more efficient synthetic procedure has been developed for the preparation of [CpRuCl(PMe^iPr_2)$_2$], and details are given. IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. Raman spectra were recorded at the Serveis Cientifico-Tècnics, Universitat de Barcelona, using a Jobin-Yvon T64000 dispersive spectrometer equipped with a Coherent Innova 306 argon laser as excitation source (λ = 514 nm). NMR spectra were taken on a Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in parts per million from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). Microanalysis was performed by the Serveis Científico-Tècnics, Universitat de Barcelona. The nitrogen content was found to be low or even very low in several cases, due to the lability of the N_2 ligand in these compounds. Therefore, the found and calculated percentage figures do not match for nitrogen content in these cases, whereas carbon and hydrogen microanalysis is acceptable.

[CpRuCl(PMe^{i}Pr$_2$)$_2$]. A solution of $RuCl_3$ was made by boiling hydrated ruthenium trichloride (0.5 g, ca. 1.9 mmol) in ethanol (5 mL). The insoluble matter, if any, was separated from the liquor by decantation. The solution was cooled, and freshly cracked cyclopentadiene (1 mL, excess) was added. This mixture was added dropwise to a refluxing solution containing PMe^iPr_2 (1.2 mL, 7.9 mmol) and cyclopentadiene (1 mL, excess) in EtOH (80 mL). Once the addition was completed, the reaction mixture was heated under reflux for another 2 h. During this time, the color changed from dark green to orange-red. After this time, the solvent was removed in vacuo, and the residue extracted with petroleum ether (50 mL). Concentration (to ca. 10 mL) and cooling to −20 °C gave bright orange-red needle-shaped crystals, which were filtered off and dried in vacuo. Yield: 0.6 g, 67%. The spectral properties of this compound were coincident with those previously reported.[5]

[{CpRu(P)$_2$}$_2$(μ-N$_2$)][BAr′$_4$]$_2$ [(P)$_2$ = dippe 1a; (PEt$_3$)$_2$ 1b; (PMe^{i}Pr$_2$)$_2$ 1c]. To a solution of the corresponding derivative [CpRuCl(P)$_2$] [(P)$_2$ = dippe for **1a**, $(PEt_3)_2$ for **1b**, or $(PMe^iPr_2)_2$ for **1c**] (0.5 mmol) in fluorobenzene (10 mL) under argon was added solid NaBAr′$_4$ (0.44 g, 0.5 mmol). Dinitrogen (6 mL, ca. 0.25 mmol) was injected through the reaction mixture using a gas-tight syringe. The mixture was stirred for 15 min at room temperature. Sodium chloride was removed by filtration through Celite. The resulting solution was layered with petroleum ether and left standing undisturbed at room temperature. Well-formed yellow crystals were obtained by slow diffusion of the petroleum ether into the fluorobenzene solution. These crystals were isolated by cannulating off the supernatant liquor and dried under an argon stream. Yield: 60−70%. **1a**: Anal. Calcd for $C_{102}H_{97}N_2B_2F_{48}P_4Ru_2$: C, 46.9; H, 3.72; N, 1.07. Found: C, 46.7; H, 3.82; N, 0.90. Raman: ν(N≡N) 2050 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.21 (m, P(CH(CH_3)$_2$)$_2$), 1.87 (m, PCH_2), 2.25 (double multiplet, P(CH(CH$_3$)$_2$)$_2$), 5.08 (s, RuC$_5H_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2): δ 92.2 (s). **1b**: Anal. Calcd for $C_{98}H_{94}N_2B_2F_{48}P_4Ru_2$: C, 46.0; H, 3.67; N, 1.09. Found: C, 46.2; H, 3.62; N, 0.50. Raman: ν(N≡N) 2064 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.12 (m, P(CH$_2$CH_3)$_3$), 1.80 (double multiplet, P(CH_2CH$_3$)$_3$), 5.01 (s, RuC$_5H_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2): δ 30.9 (s). **1c**: Anal. Calcd for $C_{102}H_{102}N_2B_2F_{48}P_4Ru_2$: C, 46.8; H, 3.90; N, 1.07. Found: C, 46.7; H, 3.91; N, 0.44. Raman: ν(N≡N) not observed due to decomposition. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.19 (m, P(CH(CH_3)$_2$)$_2$), 1.36 (m, PCH_3), 2.15 (double multiplet, P(CH(CH$_3$)$_2$)$_2$), 5.09 (s, RuC$_5H_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2): δ 37.5 (s).

[CpRu(N$_2$)(P)$_2$][BAr′$_4$] [(P)$_2$ = dippe 2a; (PMe^{i}Pr$_2$)$_2$ 2c; (PMe^{i}Pr$_2$)(PPh$_3$) 2d]. These compounds were obtained in a fashion analogous to that for the dinitrogen-bridged derivatives **1a**−**1c**, starting from [CpRuCl(P)$_2$] [(P)$_2$ = dippe for **2a**, $(PMe^iPr_2)_2$ for **2c**, or (PMe^iPr_2)(PPh_3) for **2d**] (0.25 mmol) and NaBAr′$_4$ (0.22 g, 0.25 mmol) in fluorobenzene under a dinitrogen atmosphere. Yield: ca. 80% in all cases. **2a**: Anal. Calcd for $C_{51}H_{49}N_2BF_{24}P_2Ru$: C, 46.4; H, 3.72; N, 2.12. Found: C, 46.1; H, 3.69; N, 1.87. IR: ν(N≡N) 2158 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.21 (m, P(CH(CH_3)$_2$)$_2$), 1.87 (m, PCH_2), 2.25 (double multiplet, P(CH(CH$_3$)$_2$)$_2$), 5.16 (s, RuC$_5H_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2): δ 92.2 (s). **2c**: Anal. Calcd for $C_{51}H_{51}N_2BF_{24}P_2Ru$: C, 46.3; H, 3.86; N, 2.12. Found: C, 46.5; H, 3.67; N, 1.70. IR: ν(N≡N) 2164 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.20 (m, P(CH(CH_3)$_2$)$_2$), 1.36 (m, PCH_3), 2.20 (double multiplet, P(CH(CH$_3$)$_2$)$_2$), 5.08 (s, RuC$_5H_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2): δ 37.5 (s). **2d**: Anal. Calcd for $C_{62}H_{49}N_2BF_{24}P_2Ru$: C, 51.3; H, 3.38; N, 1.93. Found: C, 51.1; H, 3.38; N, 0.43. IR: ν(N≡N) 2177 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 243 K): δ 0.51 (m, PCH_3), 0.80−1.20 (m, P(CH(CH_3)$_2$)$_2$), (double multiplet, P(CH(CH$_3$)$_2$)$_2$), 4.87 (s, RuC$_5H_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 243 K): δ 43.9 (d, $^2J_{PP}$ = 31.5 Hz, PMe^iPr_2), 37.3 (d, $^2J_{PP}$ = 31.5 Hz, PPh_3).

[CpRu(PMe^{i}Pr$_2$)$_3$][BAr′$_4$], 3. A solution of [CpRuCl(PMe^iPr_2)$_2$)] (0.12 g, 0.25 mmol) in fluorobenzene (6 mL) was

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Table 1. Summary of Crystallographic Data for Compounds 1a, 1b, 2a, 3, and 4

	1a (with FPh)	**1b** (with 2 FPh)	**2a**	**3**	**4** (with 2FPh)
formula	$C_{108}H_{103}B_2F_{49}N_2P_4Ru_2$	$C_{110}H_{104}B_2F_{50}N_2P_4Ru_2$	$C_{51}H_{49}BF_{24}N_2P_2Ru$	$C_{58}H_{68}BF_{24}P_3Ru$	$C_{75}H_{59}BF_{26}P_2Ru$
fw	2707.56	2751.60	1319.74	1425.91	1616.03
T (K)	223(2)	213(2)	223(2)	223(2)	213(2)
cryst size (mm)	0.80 × 0.60 × 0.32	0.8 × 0.7 × 0.4	0.46 × 0.42 × 0.38	0.72 × 0.68 × 0.40	0.7 × 0.4 × 0.3
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*1 (no. 2)	*P*1 (no. 2)	$P2_1/n$ (no. 14)	C*c* (no. 9)	$P2_1/c$ (no. 14)
cell params	$a = 13.986(4)$ Å $b = 14.321(4)$ Å $c = 15.273(5)$ Å $\alpha = 83.25(1)°$ $\beta = 69.96(1)°$ $\gamma = 85.60(1)°$	$a = 13.310(3)$ Å $b = 13.702(3)$ Å $c = 17.120(3)$ Å $\alpha = 83.76(1)°$ $\beta = 73.03(1)°$ $\gamma = 81.54(1)°$	$a = 12.391(4)$ Å $b = 35.677(12)$ Å $c = 12.885(4)$ Å $\beta = 90.01(1)°$	$a = 21.264(9)$ Å $b = 15.092(6)$ Å $c = 20.992(9)$ Å $\beta = 106.06(1)°$	$a = 23.172(12)$ Å $b = 12.868(7)$ Å $c = 25.179(13)$ Å $\beta = 105.85(3)°$
volume (Å^3)	2852(2)	2947(1)	5696(3)	6474(5)	7222(7)
Z	1	1	4	4	4
ρ_{calc} (g cm^{-3})	1.577	1.551	1.539	1.463	1.486
μ(Mo Kα) (cm^{-1})	4.49	4.37	4.47	4.22	3.71
F(000)	1364	2772	2656	2904	3264
max. and min. transmn factors	0.83−0.74	1.000−0.906	0.894−0.756	0.86−0.80	1.000−0.912
θ range for data collection (deg)	1.92 to 30.00	1.25 to 30.00	1.74 to 30.00	1.68 to 27.50	1.68 to 27.50
no. of reflns collected	52 172	43 201	82 786	39 811	130 804
no. of unique reflns	16 347 (R_{int}=0.017)	16 821 (R_{int}=0.020)	16 486 (R_{int}=0.039)	14 831 (R_{int}=0.019)	16 564 (R_{int}=0.057)
no. of obsd reflns ($I > 2\sigma_I$)	14 834	13 390	13 778	12 962	12 147
no. of params	758	816	773	886	970
final R1, wR2 values ($I > 2\sigma_I$)	0.0364, 0.0963	0.0648, 0.1614	0.0639, 0.1513	0.0469, 0.1193	0.0452, 0.1076
final R1, wR2 values (all data)	0.0409, 0.1020	0.0809, 0.1796	0.0754, 0.1607	0.0561, 0.1311	0.0707, 0.1240
residual electron density peaks (e Å^{-3})	+0.924/−0.64	+1.624/−1.074	+0.77/−0.72	+0.47/−0.86	+0.694/−0.564

treated with a slight excess over the stoichiometric amount of PMe^{i}Pr$_2$. Upon stirring for a few minutes at room temperature, NaBAr′$_4$ (0.22 g, 0.25 mmol) was added. A color change to yellow was observed. The mixture was stirred for 15 min. Sodium chloride was removed by filtration through Celite. The filtrate was layered with petroleum ether and left undisturbed at room temperature. Yellow crystals were obtained by slow diffusion of petroleum ether into the fluorobenzene, which were separated from the supernatant liquor and dried in an argon stream. Yield: 0.21 g, 60%. Anal. Calcd for $C_{58}H_{68}BF_{24}P_3Ru$: C, 48.8; H, 4.77. Found: C, 49.0; H, 4.79. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.21 (m, P(CH(C*H*$_3$)$_2$)$_2$), 1.35 (m, PC*H*$_3$), 2.09 (double multiplet, P(C*H*(CH$_3$)$_2$)$_2$), 4.94 (s, RuC$_5$*H*$_5$). ^{31}P{^{1}H} NMR (161.89 MHz, CD_2Cl_2): δ 32.2 (s).

[CpRu(PMe^{i}Pr$_2$)(η^3-PPh$_3$)][BAr′$_4$], 4. To a solution of [CpRuCl(PMe^{i}Pr$_2$)(PPh$_3$)] (0.5 g, 0.84 mmol) in fluorobenzene (10 mL) under argon was added solid NaBAr′$_4$ (0.74 g, 0.84 mmol). The mixture was stirred for 15 min at room temperature. Sodium chloride was removed by filtration through Celite. The resulting solution was layered with petroleum ether and 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 and dried under an argon stream. The crystals lose fluorobenzene of crystallization (they contain 2 fluorobenzene molecules per complex cation) almost immediately and usually crumble when dried. Yield: 0.89 g, 75%. Anal. Calcd for $C_{62}H_{49}BF_{24}P_2Ru$: C, 52.3; H, 3.44. Found: C, 51.9; H, 3.34. ^{1}H NMR (400 MHz, CD_2Cl_2, 243 K): δ 0.50−1.30 (m br, PC*H*$_3$, P(CH(C*H*$_3$)$_2$)$_2$), 2.10 (m, P(C*H*(CH$_3$)$_2$)$_2$), 4.38 (RuC$_5$*H*$_5$), 6.17, 6.26 (m, η^3-P(C$_6$*H*$_5$), 7.46 t, 7,29 m, 7.65 m (P(C$_6$*H*$_5$)). ^{31}P{^{1}H} NMR (161.89 MHz, CD_2Cl_2, 243 K): δ 36.8 (d, $^2J_{PP}$ = 39.1 Hz), 48.9 (d, $^2J_{PP}$ = 39.1 Hz). ^{13}C{^{1}H} NMR (100.58 MHz, CD_2Cl_2, 298 K): δ 6.6 (d, J_{CP} = 61.5 Hz, P*C*H$_3$), 14.4, 14.5, 15.2 (s, P(CH(*C*H$_3$)$_2$)$_2$), 24.9 (d, J_{CP} = 66.8 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 82.1 (Ru*C*$_5$H$_5$), 85.4 (d, J_{CP} = 7.7 Hz, η^3-P(*C*$_6$H$_5$)), 87.6 (d, J_{CP} = 9.4 Hz, η^3-P(*C*$_6$H$_5$)), 128.6 d, 129.3 d, 131.7 t, 132.2 s, 133.7 d (P(*C*$_6$H$_5$)).

X-ray Structure Determinations. Crystals of **1a**, **1b**, **2a**, **3**, and **4** were obtained by slow diffusion of petroleum ether into fluorobenzene solutions. 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 = 0.71073 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 applied. All structures were solved by direct methods using the program SHELXS97.[14] Structure refinement on F^2 was carried out with program SHELXL97.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. In four of the five compounds the CF$_3$ groups showed high rotatory motion about the C−CF$_3$ bond axes or a corresponding orientation disorder. Where necessary, this was taken into account by refining CF$_3$ groups split into two orientations, of which the predominanting was calculated with anisotropic temperature factors and the subordinate one with isotropic temperature factors. Salient crystallographic data are summarized in Table 1; further details are given in the Supporting Information.

Results and Discussion

In an attempt to obtain the cationic coordinatively unsaturated derivatives [CpRu(P)$_2$][BAr′$_4$] [(P)$_2$ = dippe, (PEt$_3$)$_2$, (PMe^{i}Pr$_2$)$_2$], we carried out the reaction of the corresponding complexes [CpRuCl(P)$_2$] with Na[BAr′$_4$] in fluorobenzene under an argon atmosphere. We had previously noticed during the reaction of the related systems [Cp*RuCl(P)$_2$] with Na[BAr′$_4$] in fluorobenzene

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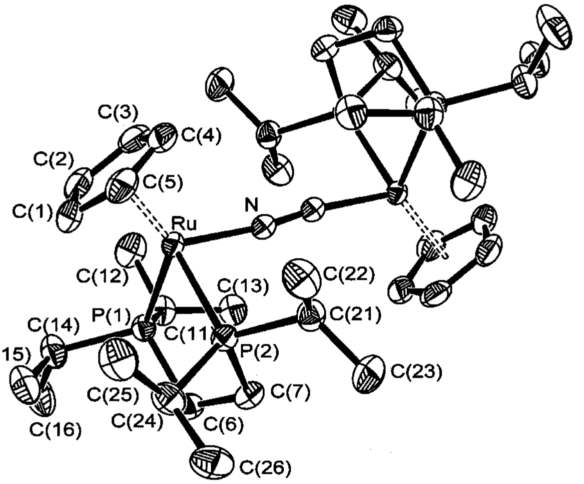

Figure 1. ORTEP drawing (50% thermal ellipsoids) of the cation $[\{CpRu(dippe)\}_2(\mu\text{-}N_2)]^{2+}$ in complex **1a**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru−C(1) 2.199(2); Ru−C(2) 2.233(2); Ru−C(3) 2.243(2); Ru−C(4) 2.250(2); Ru−C(5) 2.231(2); Ru−P(1) 2.3306(8); Ru−P(2) 2.3361(7); Ru−N 1.980(1); N−N#1 1.118(3); P(1)−Ru−P(2) 82.60(2); Ru−N1−N#1 170.7(2).

under argon the immediate development of a deep blue color, indicative of the formation of the 16-electron cationic complexes $[Cp^*Ru(P)_2][BAr'_4]$ in the reaction mixture.[12] However, no blue color was observed during the reaction of the cyclopentadienyl derivatives. Instead, clear yellow or yellow-orange solutions were obtained upon removal of sodium chloride from the mother liquor by filtration through Celite. Yellow crystals were obtained by slow diffusion of petroleum ether into these solutions under an argon atmosphere. Microanalysis indicated the presence of small but significant amounts of nitrogen in these materials (less than 1%). However, no band in the IR spectra attributable to $\nu(N_2)$ in a terminal dinitrogen complex was detected. Rather unexpectedly, X-ray structure analysis for the dippe and PEt_3 derivatives showed them to be binuclear dinitrogen-bridged complexes, namely, $[\{CpRu(dippe)\}_2(\mu\text{-}N_2)][BAr'_4]_2$, **1a**, and $[\{CpRu(PEt_3)_2\}_2(\mu\text{-}N_2)][BAr'_4]_2$, **1b**. Likewise, a formulation as $[\{CpRu(PMe^iPr_2)\}_2(\mu\text{-}N_2)][BAr'_4]_2$, **1c**, can be proposed for the PMe^iPr_2 derivative. ORTEP[16] diagrams of the complex cations $[\{CpRu(dippe)\}_2(\mu\text{-}N_2)]^{2+}$ and $[\{CpRu(PEt_3)_2\}_2(\mu\text{-}N_2)]^{2+}$ are shown in Figures 1 and 2, respectively. Both dinitrogen complexes crystallized as fluorobenzene solvates, in the form of **1a**·FPh and **1b**·2 FPh. The structure of the complex cations can be described as a centrosymmetrical arrangement of $\{[CpRu(P)_2]^+\}$ moieties linked through a dinitrogen molecule. The crystallographic center of symmetry lies in the midpoint of the N−N bond, making equivalent the two ruthenium sites. Each ruthenium adopts the typical three-legged piano stool geometry found for other complexes that contain the cyclopentadienyl bis(phospine) auxiliary fragments.[1−4,8] The dinitrogen ligand is linearly assembled to the two ruthenium atoms, as indicated by the value of the angle Ru−N1−N# of 170.7(2)° for **1a** and 172.3(3)° for **1b**. The two nitrogen atoms and the two ruthenium atoms are contained in the same plane, as a result of the center of symmetry. The Ru−N bond distances are ca. 1.98 Å for both compounds, whereas the N1−N# separations are 1.118(3) Å in the case of **1a** and 1.114(5) Å for **1b**. These values compare well with the N−N bond distances recently reported for the dinitrogen-bridged complexes $[\{$*mer,trans*-$RuCl_2(\mathbf{NN'N})\}_2(\mu\text{-}N_2)]$ (N−N 1.110(3) Å; **NN′N** = 2,6-bis[(dimethylamino)methyl]pyridine)[17] and $[\{RuH_2(N_2)(P^iPr_3)_2\}_2(\mu\text{-}N_2)]$ (bridging N−N 1.113(2) Å; terminal N−N 1.105(2) Å).[18] In the complex $[\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)][BF_4]_2$ the N−N separation was found to be 1.124 Å.[19] In all cases, the N−N separation is slightly longer than the bond length of 1.0977 Å found for the free N_2 molecule.[20] The main difference between the structures of **1a** and **1b** lies in the value of the P1−Ru−P2 angle (82.60(2)° versus 95.42(4)°), which is smaller in the case of the dippe derivative due to the "bite angle" imposed for the chelating nature of the phosphine ligand. All other bond distances and angles in the two complexes are in the expected range, being unexceptional. Consistently with the centrosymmetrical nature of the binuclear dinitrogen complex cations, the $\nu(N_2)$ band is inactive in the IR, but active in Raman. Thus, the Raman spectrum of complexes **1a** and **1b** shows medium-strong bands at 2050 and 2064 cm^{-1}, respectively. Complex **1c** seems to be more labile and was destroyed by the action of the laser, so its Raman spectrum could not be recorded. It appears that, at variance with their Cp*Ru counterparts, the 16-electron complexes $[CpRu(P)_2]^+$ $[(P)_2 = \text{dippe}, (PEt_3)_2, (PMe^iPr_2)_2]$ are exceedingly reactive, having an enormous avidity

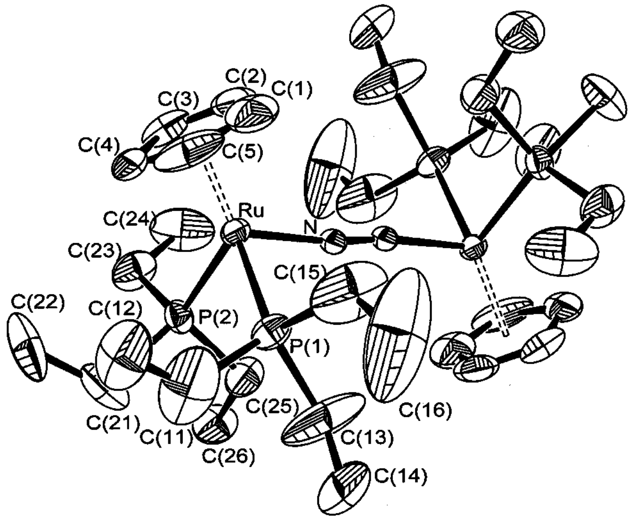

Figure 2. ORTEP drawing (50% thermal ellipsoids) of the cation $[\{CpRu(PEt_3)_2\}_2(\mu\text{-}N_2)]^{2+}$ in complex **1b**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru−C(1) 2.208(5); Ru−C(2) 2.222(5); Ru−C(3) 2.223(5); Ru−C(4) 2.171(5); Ru−C(5) 2.190(5); Ru−P(1) 2.334(1); Ru−P(2) 2.351(1); Ru−N 1.977(3); N−N#1 1.114(5); P(1)−Ru−P(2) 95.42(4); Ru−N1−N#1 172.3(3).

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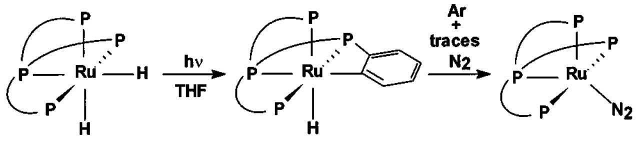
for dinitrogen. Thus, upon generation by halide abstraction, the coordinatively unsaturated complex cations react immediately with the small amount of N_2 present in the argon used as protective atmosphere (ca. 2 ppm). The dinitrogen-bridged complexes **1a**−**1c** were isolated in a reproducible manner as the only species resulting from the reaction, in ca. 50% yield under these conditions. The reaction of highly reactive coordinatively unsaturated complexes with trace amounts of N_2 present in high-purity argon or even helium to give dinitrogen complexes has been reported by other authors. Thus, photolysis of $[RuH_2(PP_3)]$ ($PP_3 = P(CH_2CH_2PPh_2)_3$)[21] in THF under argon atmospheres (BOC Pureshield Argon, 99.995%) yielded the terminal Ru^0 dinitrogen complex $[Ru(N_2)(PP_3)]$, albeit in small quantities.[22] This was attributed to the efficient scavenging of N_2 by the cyclometalated complex of formula $[Ru(PP_3)]$ formed upon irradiation of the dihydride:[22]



The complex $[Mo(CO)(depe)_2]$ (depe = 1,2-bis(diethylphosphino)ethane)[23] is stabilized by an agostic interaction with one of the CH_3 groups of the depe ligand. This compound is so reactive toward dinitrogen that both in solution and in the solid state it can scavenge traces of dinitrogen inside a glovebox operated under a helium atmosphere to give the bridging dinitrogen complex $[\{Mo(CO)(depe)_2\}_2(\mu\text{-}N_2)]$.[23] It therefore appears that the moieties $\{[CpRu(P)_2]^+\}$ possess N_2-scavenging abilities similar to those of $[Ru(PP_3)]$ and $[Mo(CO)(depe)_2]$. The procedure for the synthesis of the N_2-bridged complexes **1a**−**1c** can be standarized by introducing the stoichiometric amount of N_2 into the reaction mixture via syringe, resulting in 60−70% yield of isolated product.

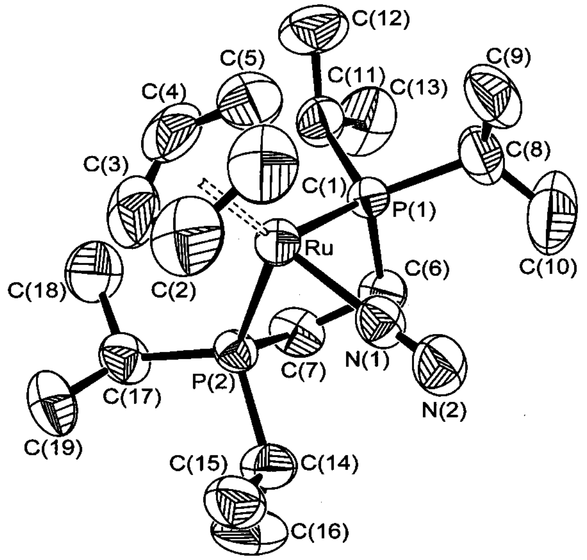


Figure 3. ORTEP drawing (50% thermal ellipsoids) of the cation $[CpRu(N_2)(dippe)]^+$ in complex **2a**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru−C(1) 2.216(4); Ru−C(2) 2.228(5); Ru−C(3) 2.220(4); Ru−C(4) 2.202(4); Ru−C(5) 2.224(4); Ru−P(1) 2.327(1); Ru−P(2) 2.326(1); Ru−N(1) 1.961(3); N(1)−N(2) 1.087(4); P(1)−Ru−P(2) 83.86(3); Ru−N(1)−N(2) 175.8(4).

We have previously reported the preparation of some labile terminal dinitrogen half-sandwich ruthenium complexes of the type $[(C_5R_5)Ru(P_2)][BPh_4]$ [R = H, Me, P_2 = dippe; R = Me, $P_2 = (PEt_3)_2$]. Attempts made to purify these complexes led to dinitrogen loss in all cases. However, the use of $Na[BAr'_4]$ as halide scavenger and anion for crystallization has made possible the standarization of the procedure for the synthesis of cationic dinitrogen complexes of ruthenium. Thus, the reaction of $[CpRuCl(P)_2]$ with $Na[BAr'_4]$ in fluorobenzene under N_2 yielded the terminal dinitrogen complexes $[CpRu(N_2)(P)_2][BAr'_4]$ [$(P)_2$ = dippe **2a**, $(PMe^iPr_2)_2$ **2c**, $(PMe^iPr_2)(PPh_3)$ **2d**]. The reaction of $[CpRuCl(PEt_3)_2]$ with $Na[BAr'_4]$ under dinitrogen failed to give $[CpRu(N_2)(PEt_3)_2][BAr'_4]$, and the dinitrogen-bridged complex **1b** was obtained instead. As expected, all terminal dinitrogen complexes display one strong $\nu(N_2)$ band in their IR spectra, in the range 2150−2180 cm^{-1}. It is interesting to note that the ^1H and $^{31}P\{^1H\}$ NMR spectra of the bridging dinitrogen complexes **1a** and **1c** and those of the terminal dinitrogen complexes **2a** and **2c** are essentially identical. This seems logical, given the fact that the chemical environment around each ruthenium atom remains the same, irrespectively of being a bridging or a terminal dinitrogen complex. Compounds **1a** and **2a** react slowly with dichloromethane, furnishing blue solutions. These blue solutions display broad features in its ^1H NMR spectrum, indicative of the presence of paramagnetic species. No attempt was made to identify these species. The X-ray crystal structure of **2a** was determined, to compare with the structure of its dinitrogen-bridged counterpart. An ORTEP view of the complex cation is shown in Figure 3. It shows a “three-legged piano stool” structure, with the dinitrogen ligand bound in the end-on manner, resembling very much the structure of the homologous iron complex cation $[CpFe(N_2)(dippe)]^+$.[24] All structural parameters within the complex $[CpRu(N_2)(dippe)]^+$, with the exception of those involving the N_2-ligand, are essentially identical to those found for the bridging dinitrogen derivative **1a**. Thus, the Ru−N1−N2 angle of 175.8(4)° indicates an almost perfectly linear Ru−N_2 assembly, with a Ru−N1 separation of 1.961(3) Å and a N1−N2 bond length of 1.087(4) Å. These bond distances compare well with those reported for other terminal Ru−N_2 complexes such as $[TpRu(N_2)(PEt_3)_2][BPh_4]$ (Tp = hydrotris(pyrazolyl)borate(1−); Ru−N1 1.910(2) Å, N1−N2 1.010(2) Å)[7] or $[TpRu(N_2)(PN)][CF_3SO_3]$ (PN = $Ph_2PCH_2CH_2NMe_2$; Ru−N1 1.943(4) Å, N1−N2 1.097(5) Å).[25] Whereas in terminal dinitrogen complexes the N−N separation is essentially identical to that corresponding to the free N_2 molecule,[26] in the bridging N_2 complexes it is slightly longer (ca. 0.1 Å). It has been shown by EHMO calcula-

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tions that upon binding to ruthenium, there is a reinforcement of the σ-bonding and a weakening of the π-bonding in the N_2 ligand.[25] These opposite effects lead to almost no change in the N−N bond distance upon coordination. However, when the dinitrogen ligand acts as a bridge between two ruthenium centers, there is an overall weakening effect, which leads to a small elongation of the N−N bond, consistent with back-donation of electron density from Ru^{II} to N_2.

Despite the great affinity of the $\{[CpRu(P)_2]^+\}$ moieties for N_2, we kept searching for coordinatively unsaturated species. In one of our earlier attempts to prepare the 16-electron complex $[CpRu(PMe^iPr_2)_2]$-$[BAr'_4]$ by reaction of $[CpRuCl(PMe^iPr_2)_2]$ with Na-$[BAr'_4]$ in fluorobenzene under argon, we isolated a yellow crystalline material, which was identified as the tris(phosphine) derivative $[CpRu(PMe^iPr_2)_3][BAr'_4]$, **3**. This material was formed in the reaction mixture due possibly to the presence of free PMe^iPr_2 accompanying the starting material $[CpRuCl(PMe^iPr_2)_2]$, since it had been obtained following our previously published method: thermal substitution of PPh_3 in $[CpRuCl$-$(PPh_3)(PMe^iPr_2)]$ by PMe^iPr_2 followed by column chromatography.[5] We have now modified the procedure for the synthesis of $[CpRuCl(PMe^iPr_2)_2]$, which is conveniently prepared by direct reaction of hydrated ruthenium trichloride with cyclopentadiene and PMe^iPr_2 in boiling ethanol, being isolated as a crystalline material void of free phosphine impurities. Hence, **3** can be synthesized in good yield by reaction of $[CpRuCl$-$(PMe^iPr_2)_2]$ with 1 equiv of PMe^iPr_2 and $Na[BAr'_4]$ in fluorobenzene. It is rather surprising the fact that three bulky phosphine ligands such as PMe^iPr_2 can bind simultaneously to the same ruthenium atom, adopting a *fac*-stereochemistry. Furthermore, we have been unable to generate the analogous tris(phosphine) complex $[Cp^*Ru(PMe^iPr_2)_3][BAr'_4]$ by reaction of the genuine 16-electron complex $[Cp^*Ru(PMe^iPr_2)_2][BAr'_4]$[12] with an excess of PMe^iPr_2. Although Cp* is more sterically demanding than Cp, it seems that the stabilization of the coordinatively unsaturated Cp*Ru species is due to electronic rather than steric reasons. We recently reached a similar conclusion concerning the stabilization of the neutral 16-electron complex $[Cp^*RuCl(PMe^iPr_2)]$ versus the 18-electron derivative $[Cp^*RuCl(PMe^iPr_2)_2]$.[5] The X-ray crystal structure of **3** was determined. An ORTEP view of the complex cation is shown in Figure 4. Again, the complex cation adopts a "three-legged piano stool structure", with the three phosphine ligands in a *fac*-disposition around ruthenium. The Ru−P separations are in the range expected, being unexceptional, whereas the P−Ru−P angles are all close to 95°. To minimize the steric pressure, the substituent groups of each phosphine adopt a particular orientation: the methyl groups of each of the PMe^iPr_2 ligands are all pointing down in the same direction, away from the ruthenium. The isopropyl substituents also point away from the ruthenium, but toward the Cp plane. The result is a quite symmetrical arrangement of the phosphines around the metal, which is consistent with a "perfect fit" of the three ligands despite the bulk of the substituents on the phosphorus atoms.

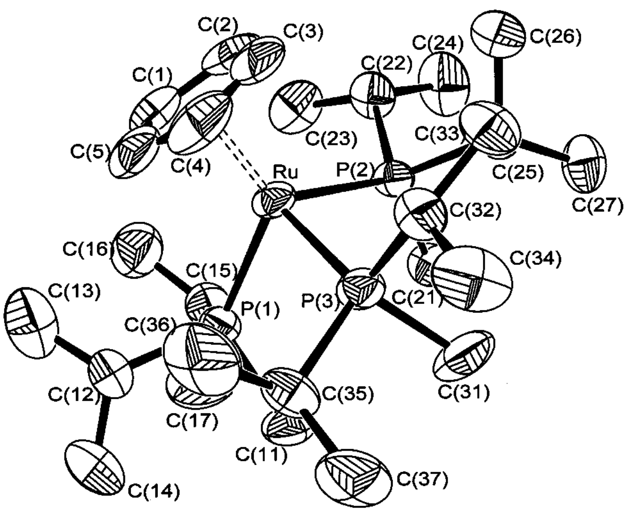

Figure 4. ORTEP drawing (50% thermal ellipsoids) of the cation $[CpRu(PMe^iPr_2)_3]^+$ in complex **3**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru−C(1) 2.245(5); Ru−C(2) 2.241(5); Ru−C(3) 2.222(5); Ru−C(4) 2.246(6); Ru−P(3) 2.366(2); Ru−C(5) 2.240(5); Ru−P(1) 2.368(2); Ru−P(2) 2.356(1); P(1)−Ru−P(2) 95.12(4); P(2)−Ru−P(3) 94.85(4); P(1)−Ru−P(3) 94.47(6).

Although the terminal dinitrogen complex $[CpRu$-$(N_2)(PPh_3)(PMe^iPr_2)][BAr'_4]$ has been prepared in this work, the reaction of $[CpRuCl(PPh_3)(PMe^iPr_2)]$ with Na-$[BAr'_4]$ and the stoichiometric amount of N_2 in fluorobenzene under argon did not produce the dinitrogen-bridged complex $[\{CpRu(PPh_3)(PMe^iPr_2)\}_2(\mu\text{-}N_2)][BAr'_4]_2$. Instead, a red crystalline compound of formula $[CpRu$-$(PPh_3)(PMe^iPr_2)][BAr'_4]$, **4**, was obtained. The ^1H NMR spectrum of this material in CD_2Cl_2 under Ar displayed two multiplet resonances at 6.17 and 6.26 ppm, apart from signals due to Cp, PMe^iPr_2, and the aromatic protons of PPh_3. The $^{31}P\{^1H\}$ consisted of broad features, being temperature-dependent. At 243 K, two rather broad doublets were observed in the $^{31}P\{^1H\}$ NMR spectrum, whereas the ^1H spectrum remains essentially identical to that recorded at 298 K. The ^{31}P-$\{^1H\}$ NMR spectrum becomes featureless at 363 K (using $C_2D_2Cl_4$ as solvent). However, even at this temperature the ^1H NMR spectrum is essentially identical to that recorded at 298 K. Some of these resonances had been previously observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra of the terminal dinitrogen complex **2d**. The ^1H NMR resonances around 6.2 ppm were initially attributed to an agostic interaction of the metal with *ortho*-hydrogens of the phenyl groups of the PPh_3 ligand, as it is known to occur in $[RuCl_2(PPh_3)_3]$.[27] However, an X-ray structure analysis performed on the fluorobenzene solvate **4**·2 FPh proved this structural assignment to be incorrect. Instead, a very rare η^3-coordination mode for the PPh_3 ligand was found. An ORTEP view of the complex cation $[CpRu(\eta^3\text{-}PPh_3)(PMe^iPr_2)]^+$ is shown in Figure 5. The structure can be described as a bent "two-legged piano stool" in which the vacant coordination position is occupied by one of the C═C

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[26] For X-ray structures of terminal Ru−N_2 complexes see: Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1997**, *16*, 1253. Jia, G.; Meek, D. W.; Gallucci, J. C. *Inorg. Chem.* **1991**, *30*, 403. Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727. Camenzind, M. J.; James, B. R.; Dolphin, D.; Sparapany, J. W.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 3054.

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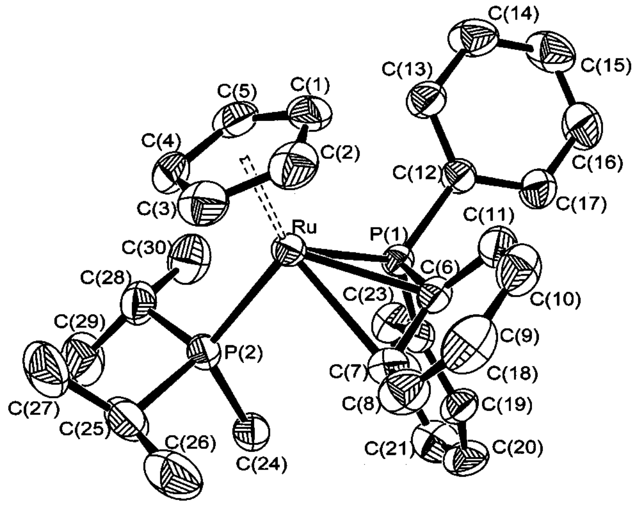
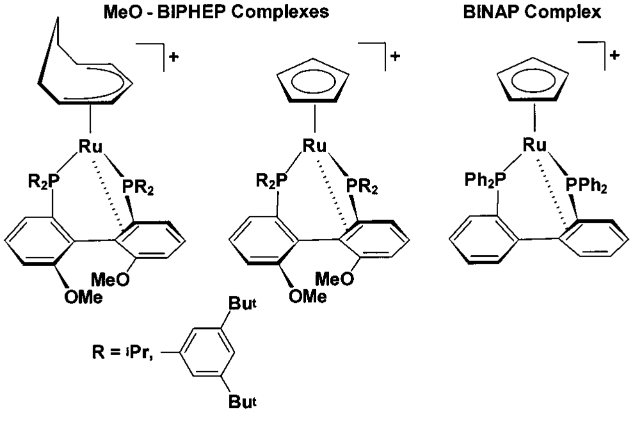


Figure 5. ORTEP drawing (50% thermal ellipsoids) of the cation $[CpRu(\eta^3{-}PPh_3)(PMe^iPr_2)]^+$ in complex **4**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru−C(1) 2.201(3); Ru−C(2) 2.193(3); Ru−C(3) 2.214(3); Ru−C(4) 2.195(3); Ru−C(5) 2.191(3); Ru−P(1) 2.2951(11); Ru−P(2) 2.3717(12); Ru−C(6) 2.371(3); Ru−C(7) 2.459(3); P(1)−C(6) 1.799(3); C(6)−C(7) 1.420(4); C(6)−C(11) 1.427(4); C(7)−C(8) 1.414(4); C(8)−C(9) 1.366(5); C(9)−C(10) 1.406(5); C(10)−C(11) 1.362(4); P(1)−Ru−P(2) 96.81(4); P(1)−C(6)−C(3) 116.9(2); Ru−P(1)−C(6) 69.6(1); Ru−P(1)−C(12) 124.1(1); Ru−P(1)−C(18) 130.4(1).

bonds of a phenyl substituent of the PPh_3 ligand. In this way the system attains the 18-electron configuration. Thus, the PPh_3 ligand is acting as a chelating ligand, which binds to the metal through the phosphorus atom and simultaneously through a π-interaction involving two carbon atoms of one of the phenyl rings, in a fashion which resembles the coordination of π-allyls. The ruthenium atom is located out of the plane of the phenyl ring, and unsymmetrically bonded to the carbon atoms C(6) (Ru−C(6) 2.371(3) Å) and C(7) (Ru−C(7) 2.459(3) Å). This type of η^3-coordination greatly distorts the PPh_3 ligand, as suggested by the value of 69.56(10)° for the angle Ru−P(1)−C(6) in comparison with the values of 124.1(1)° and 130.4(1)° found respectively for the angles Ru−P(1)−C(12) and Ru−P(1)−C(18). The dihedral angle formed by the plane defined by the atoms Ru−C(6)−C(7) and the plane of the phenyl ring is 58.2°. These structural features match very well those reported very recently for the complex $[CpMo(CO)_2(\eta^3\text{-}PPh_3)][BAr'_4]$,[28] which constitutes the first structurally characterized example of a complex containing a four-electron donor chelating η^3-PPh_3 ligand. By considering the molecular structure of **4**, we might attribute to the protons attached to the η^3-phenyl ring the mutiplet signals observed around 6.2 ppm in the ^1H NMR spectrum. However, and at variance with the complex $[CpMo(CO)_2(\eta^3\text{-}PPh_3)]^+$,[28] *two multiplets* are observed in our case. These multiplets at 6.17 and 6.26 ppm correlate with two doublet resonances at 85.4 and 87.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum, as shown by a 2D-HETCOR NMR experiment. It is likely that rapid phenyl ring scrambling takes place in solution. This means that all of the phenyl rings should be exchanging and participating in the η^3-interaction with the metal. As a result, all *ortho*-protons in the PPh_3 ligand should have a contribution derived from the interaction with the metal in their chemical shifts, leading to a low-frequency position in the ^1H NMR spectrum. In any case, the NMR spectra of **4** and the dynamic process responsible for their temperature dependence are rather complicated and not straightforward to figure out. Hence, our interpretation must be considered only as tentative. In ruthenium chemistry, the systems shown in Scheme 1 display a behavior closely related to that of **4**.[29−31] All these systems, which have been subjected to very detailed NMR studies[29,30] as well as to X-ray structure analysis in several instances, attain the 18-electron configuration by coordination of one of the biaryl double bonds to ruthenium. They also exhibit a dynamic behavior in solution involving double bond dissociation, and these processes have been studied by 2D-NMR exchange spectroscopy.[29,30] Thus, the coordination of the C=C bond to the metal is weak and therefore can be displaced by ligands such as N_2. In fact, it appears to occur an equilibrium between the dinitrogen complex **2d** and **4** in dichloromethane solution under dinitrogen:

Scheme 1. Ruthenium Complexes Containing Chelating Phosphine Ligands Acting as Six-Electron Donor via Coordination of One of the Biaryl Double Bonds (Refs 29−31)



$$\underset{\mathbf{2d}}{[CpRu(N_2)(PPh_3)(PMe^iPr_2)]^+} \rightleftarrows \underset{\mathbf{4}}{[CpRu(\eta^3 - PPh_3)(PMe^iPr_2)]^+} + N_2$$

At low temperature, the equilibrium is shifted to the dinitrogen complex, whereas higher temperatures favor N_2 dissociation, in analogy with what happens in the system $[CpFe(N_2)(dippe)]^+$.[24]

We can conclude that if there are aromatic substituents present in a phosphine ligand, either monodentate as PPh_3 or bidentate as BINAP or related ligands,[29−31] the stabilization of coordinatively unsaturated species by coordination of double bonds of the arene substituents becomes feasible. One of these systems is the often-invoked 16-electron $\{[CpRu(PPh_3)_2]^+\}$ fragment,[1] which

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[28] Cheng, T.-Y.; Szalda, D. J.; Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1999**, 1629.

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is involved in many catalytic transformations,[32] and it is a binding site for many small molecules. We have actually isolated a yellow glassy solid from the reaction of [CpRuCl(PPh_3)$_2$] with NaBAr′$_4$ in fluorobenzene under argon. All attempts to obtain a crystalline material have been so far unsuccessful. However, the NMR of the crude product shows two multiplet signals at 6.16 and 6.23 ppm, very much like those displayed by compound **4**. Likewise, two doublets were observed in the $^{13}C\{^1H\}$ NMR spectrum at 85.4 and 87.6 ppm in connection with the mentioned proton resonances. The $^{31}P\{^1H\}$ NMR consists of one very broad feature at room temperature, which apparently splits into two broad resonances at −85 °C. Although the material was not obtained in pure form, these data support the existence of the fragment $\{[CpRu(PPh_3)_2]^+\}$ in the form of a complex containing C═C bonds coordinated to ruthenium in the same fashion as in compound **4**, and hence it should be formulated as $[CpRu(\eta^3\text{-}PPh_3)(\eta^1\text{-}PPh_3)]^+$.

Conclusions

At variance with their Cp* counterparts, the cationic 16-electron complexes $[CpRu(P)_2]^+$ display an enormous avidity for dinitrogen, being capable of scavenging it from high-purity argon, resulting in the formation of dinitrogen-bridged complexes $[\{CpRu(P)_2\}_2(\mu\text{-}N_2)]^{2+}$, which have been isolated and structurally characterized in some instances. In most cases, the direct reaction of $[CpRu(P)_2]^+$ with N_2 leads to the corresponding terminal dinitrogen complexes $[CpRu(N_2)(P)_2]^+$. From the structural point of view, both bridging and terminal N_2 complexes have similar features, with slight differences in the N−N bond distance, which is longer in the case of a bridging dinitrogen ligand. Stabilization of 16-electron species $[CpRu(P)_2]^+$ is feasible when aromatic substituent groups are present in any of the phosphine ligands, by coordination of one of the C═C bonds of the arene substituents to the metal, as it has been observed for $[CpRu(PMe^iPr_2)(\eta^3\text{-}PPh_3)][BAr'_4]$. This unusual coordination mode is apparently preferred over the stabilization by agostic interaction for attaining the 18-electron configuration in these complexes.

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Supporting Information Available: Tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **1a**, **1b**, **2a**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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