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Synthesis and properties of hydrotris(pyrazolyl)borate (Tp) ruthenium complexes with benzophenone imine: X-ray crystal structure of $[TpRu(HN{=}CPh_2)(PEt_3)_2][BPh_4]$

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Abstract

The complexes [TpRuCl(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) and $[TpRuCl(PEt_3)_2]$ react with $HN{=}CPh_2$ and $NaBPh_4$ in MeOH affording the cationic mononuclear imine derivatives $[TpRu(HN{=}CPh_2)(dippe)][BPh_4]$ and $[TpRu(HN{=}CPh_2)(PEt_3)_2][BPh_4]$, respectively. The X-ray crystal structure of the latter has been determined. The reaction of $[TpRuCl(PMe^iPr_2)(MeCN)]$ with $HN{=}CPh_2$ led to the neutral imine derivative $[TpRuCl(PMe^iPr_2)(HN{=}CPh_2)]$, which adds a second imine ligand upon chloride dissociation affording the cationic bis(imine) complex $[TpRu(PMe^iPr_2)(HN{=}CPh_2)_2]^+$. The cationic complexes $[TpRu(HN{=}CPh_2)(dippe)][BPh_4]$ and $[TpRu(HN{=}CPh_2)(PEt_3)_2][BPh_4]$ react with $KOBu^t$ in tetrahydrofuran yielding the neutral metalated species $[TpRu(\sigma\text{-}\eta^1\text{-}C_6H_4C(Ph){=}NH)(dippe)]$ and the phenyl complex $[TpRu(\sigma\text{-}\eta^1\text{-}C_6H_5)(PEt_3)_2]$, respectively. All compounds were characterized by IR, NMR and microanalysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Imine complexes; Azavinylidene complexes; Hydrotris(pyrazolyl)borate; Ruthenium; Phosphine

1. Introduction

A great deal of chemical transformations of organic imines mediated by transitions metal complexes are known. For instance, ruthenium hydrides have shown to be efficient catalysts for the isomerization of imines via [1,3] — hydrogen shift [1], for the transfer hydrogenation of ketones and imines by isopropanol [2], or for the addition of aromatic imines at the *ortho* — C–H bonds to olefins [3]. Ruthenium complexes also catalyze the asymmetric hydrosilylation of imines [4]. On the other hand, there is a growing interest in the catalytic C=N bond formation by metal–imide mediated imine metathesis [5], which may offer important advantages over the conventional acid-catalyzed imine exchange [6]. Imines show a varied reactivity towards transition metal complexes. Reactions of aromatic imines with the in situ generated butatrienylidene ruthenium cation $[CpRu{=}C{=}C{=}C{=}CH_2(PPh_3)_2]^+$ gives complexes containing 4-ethynylquinoline or 1-azabuta-1,3-diene ligands, the latter formed presumably by a [2 + 2] cycloaddition of the $C_\gamma{=}C_\delta$ double bond of the butatrienyliene moiety to the N=C of the imine [7]. The five-coordinate osmium complex $[Os(C{\equiv}CPh)_2(CO)(P^iPr_3)_2]$ adds benzophenone imine yielding an isomeric mixture of *cis*/*trans*-$[Os(C{\equiv}CPh)_2(CO)(HN{=}CPh_2)(P^iPr_3)_2]$, which eliminates phenylacetylene thermally furnishing the *ortho*-metalated compound $[Os(C{\equiv}CPh)(CO)\{HN{=}C(Ph)C_6H_4\}(P^iPr_3)_2]$ [8]. Despite all this rich chemistry, monodentate nitrogen-bound imine complexes are rare as result of the weak Lewis basicity of the imine nitrogen atom [9]. We reported recently that the X-ray crystal structure of $[RuCl_2(CO)(HN{=}CPh_2)(PMe^iPr_2)_2]$, which was prepared by the addition of benzophenone imine to the vacant coor-

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dination site of the 16-electron compound [RuCl$_2$(CO)(PMe^{i}Pr$_2$)$_2$] [10]. In order to get a better understanding of the coordination chemistry of benzophenone imine, and its further transformations when bound to a metal center, we have studied the reactivity of a series of ruthenium phosphine complexes containing the ligand hydrotris(pyrazolyl)borate (Tp) towards HN=CPh$_2$. These TpRu compounds are binding sites for a range of small molecules including H$_2$, N$_2$ [11,12] and 1-alkynes [13,14], and provide suitable metal centers for the coordination of the weakly basic imine ligand.

2. Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethylether 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 [15], [TpRuCl(dippe)] [11], [TpRuCl(PEt$_3$)$_2$], and [TpRuCl(PMe^{i}Pr$_2$)(MeCN)] [12] were prepared according to reported procedures. IR spectra were recorded in Nujol mulls on a Perkin–Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from SiMe$_4$ (^{1}H and ^{13}C{^{1}H}) or 85% H$_3$PO$_4$ (^{31}P{^{1}H}). The phosphine protons of the dippe ligand appeared in the ^{1}H NMR spectra of the corresponding compounds as a series of overlapping multiplets in the range 0.5–3 ppm, and were not assigned. Microanalysis were carried out by Dr Manuel Arjonilla at the CSIC, Instituto de Ciencias Marinas de Andalucía.

2.1. Preparation of [TpRu(HN=CPh$_2$)(dippe)][BPh$_4$] (**1**)

To a slurry of [TpRuCl(dippe)] (0.15 g, approximately 0.25 mmol) in MeOH (15 ml) an excess of solid NaBPh$_4$ (0.3 g) and benzophenone imine (0.1 ml, excess) was added. The mixture was heated using a warm water bath for 30 min. A deep yellow color developed during this time. The reaction mixture was stirred for a further 2 h at room temperature (r.t.). Then it was concentrated to approximately half of the volume and cooled to −20°C. The yellow precipitate was filtered off, washed with ethanol and petroleum ether and dried in vacuo. Yield: 0.22 g, 85%. *Anal.* Calc. for $C_{60}H_{73}N_7B_2P_2Ru$: C, 66.9; H, 6.79; N, 9.1. Found: C, 66.6; H, 6.80; N, 8.8%. IR: ν(NH) 3310 cm^{-1}; ν(BH) 2467 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.04 t, 6.16 t, 7.57 d, 7.63 d, 7.84 d, 7.89 d ($B(C_3H_3N_2)_3$); 6.00 d, 6.88 t, 7.11 t, 7.19 t, 7.47 t ($HN{=}C(C_6H_5)_2$); 10.32 (s, br, *H*N=). ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$): δ 74.3 s. ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$): δ 18.5, 19.3, 19.5 (s, $P(CH(CH_3)_2)_2$); 20.5 m (P*C*H$_2$); 24.9, 27.2 (m, $P(CH(CH_3)_2)_2$); 105.9, 106.8, 135.4, 137.3, 144.9, 146.7 (s, $B(C_3H_3N_2)_3$); 125.9, 127.6, 127.7, 129.3, 129.7, 131.7 ($HN{=}C(C_6H_5)_2$); 187.4 (s, $HN{=}C(C_6H_5)_2$).

2.2. Preparation of [TpRu(HN=CPh$_2$)(PEt$_3$)$_2$][BPh$_4$] (**2**)

This compound was obtained following a procedure analogous to that used for the preparation of **1**, starting from [TpRuCl(PEt$_3$)$_2$]. Yield: 80%. *Anal.* Calc. for $C_{58}H_{71}N_7B_2P_2Ru$: C, 66.3; H, 6.76; N, 9.3. Found: C, 66.6; H, 6.68; N, 8.9%. IR: ν(NH) 3312 cm^{-1}; ν(BH) 2467 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.77 (m, PCH_2CH_3), 1.88 (m, PCH_2CH_3); 5.93 t, 6.08 t, 7.45 d, 7.70 d, 7.72 d, 7.97 d ($B(C_3H_3N_2)_3$); 6.05 d, 6.79 t, 7.05 m, 7.42 m ($HN{=}C(C_6H_5)_2$); 10.34 (s, br, *H*N=). ^{31}P{^{1}H} NMR: δ 22.2 s. ^{13}C{^{1}H} NMR: δ 5.2 (s, $P(CH_2CH_3)_3$); 15.9 (t, $J_{CP} = 14.8$ Hz, $P(CH_2CH_3)_3$); 102.6, 103.4, 132.8, 134.3, 141.7, 146.3 (s, $B(C_3H_3N_2)_3$); 122.0, 126.2, 126.9, 127.3, 130.1, 133.9 ($HN{=}C(C_6H_5)_2$); 196.8 (s, $HN{=}C(C_6H_5)_2$).

2.3. Preparation of [TpRuCl(HN=CPh$_2$)(PMe^{i}Pr$_2$)] (**3**)

To a solution of [TpRuCl(PMe^{i}Pr$_2$)(MeCN)] (0.15 g, approximately 0.3 mmol) in toluene (10 ml), benzophenone imine (0.1 ml excess) was added. The mixture was stirred at 70°C for 2 h. During this time, the color of the solution changed from yellow to orange and then finally red. The solvent was removed in vacuo, leaving a red oil. This oil was treated with petroleum ether and cooled to −20°C. A red–orange solid was obtained, which was filtered off and dried in vacuo. Yield: 0.12 g, 62%. *Anal.* Calc. for $C_{29}H_{38}N_7BPRu$: C, 52.5; H, 5.74; N, 14.8. Found: C, 52.6; H, 5.89; N, 14.5%. IR: ν(NH) 3206 cm^{-1}; ν(BH) 2466 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.06, 0.89, 0.92, 1.37 (m, $P(CH(CH_3)_2)_2$); 1.58 (d, $J_{HP} = 7.7$ Hz, PCH_3); 1.93, 2.11 (m, $P(CH(CH_3)_2)_2$); 5.30 t, 5.88 t, 5.90 t, 6.54 d, 7.30 d, 7.47 d, 7.55 d, 7.90 d, 8.08 d ($B(C_3H_3N_2)_3$); 6.29 d, 6.67 d, 6.80 t, 6.97 m, 7.41 d, 7.17 t ($HN{=}C(C_6H_5)_2$); 13.08 (s, br, *H*N=). ^{31}P{^{1}H} NMR: δ 40.7 s. ^{13}C{^{1}H} NMR: δ 4.45 (d, $J_{CP} = 21.7$ Hz, PCH_3); 16.3, 16.4, 17.8, 18.0 (s, $P(CH(CH_3)_2)_2$); 23.4, 28.6 (d, $J_{CP} = 21$ Hz, $P(CH(CH_3)_2)_2$); 105.6, 105.7, 106.0, 134.0, 134.1, 135.5, 142.0, 146.9, 147.1 (s, $B(C_3H_3N_2)_3$); 126.4, 128.1, 128.9, 129.1, 130.0, 138.1, 139.1 ($HN{=}C(C_6H_5)_2$), 178.9 (s, $HN{=}C(C_6H_5)_2$).

2.4. Preparation of [TpRu(HN=CPh$_2$)$_2$(PMe^{i}Pr$_2$)][BPh$_4$] (4)

A solution of **3** (0.1 g, 0.15 mmol) in MeOH (10 ml) was treated with benzophenone imine (0.1 ml, excess) and solid NaBPh$_4$ (0.3 g, excess). The mixture was heated gently using a warm water bath. After a few minutes, an orange crystalline precipitate was formed. The mixture was stirred for 12 h at r.t. The yellow–orange precipitate was filtered off, washed with ethanol and petroleum ether and dried in vacuo. Yield: 0.15 g, 84%. *Anal.* Calc. for $C_{66}H_{69}N_8B_2PRu$: C, 70.3; H, 6.12; N, 9.9. Found: C, 70.4; H, 6.03; N, 9.8%. IR: ν(NH) 3250 cm^{-1}; ν(BH) 2476 cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 0.52, 1.36 (m, $P(CH(C\mathit{H}_3)_2)_2$); 1.63 (d, $J_{HP} = 7.3$ Hz, $PC\mathit{H}_3$); 2.32 (m, $P(C\mathit{H}(CH_3)_2)_2$); 5.70 t, 6.49 t, 7.20 d, 7.68 d, 7.84 d, 8.19 d ($B(C_3\mathit{H}_3N_2)_3$); 6.42 d, 6.92 t, 7.06 d, 7.15 t, 7.40 t, 7.49 t ($HN{=}C(C_6\mathit{H}_5)_2$); 11.01 (s, br, $\mathit{H}N{=}$). $^{31}P\{^1H\}$ NMR: δ 33.7 s. $^{13}C\{^1H\}$ NMR: δ 5.7 (d, $J_{CP} = 21$ Hz, $P\mathit{C}H_3$); 17.8, 18.3 (s, $P(CH(\mathit{C}H_3)_2)_2$); 26.4 (d, $J_{CP} = 24$ Hz, $P(\mathit{C}H(CH_3)_2)_2$); 107.3, 108.4, 136.9, 138.1, 143.2, 147.1 (s, $B(\mathit{C}_3H_3N_2)_3$); 127.9, 128.7, 128.9, 129.7, 130.7, 131.8 ($HN{=}C(\mathit{C}_6H_5)_2$); 188.2 (s, $HN{=}\mathit{C}(C_6H_5)_2$).

2.5. Preparation of [TpRu{σ-η^1-$C_6H_4C(Ph){=}NH$}(dippe)] (**5**)

A solution of **1** in tetrahydrofuran was treated with an excess of solid KOBu^t. The heterogeneous mixture becomes orange gradually. It was stirred at r.t. for 15 min. Then solvent was removed in vacuo, the residue extracted with petroleum ether and the solution filtered through Celite. Volume reduction to a few milliliters using reduced pressure and cooling to −20°C gave an orange solid, which was filtered and dried in vacuo. Yield: 66%. *Anal.* Calc. for $C_{36}H_{52}N_7BP_2Ru$: C, 57.2; H, 6.88; N, 12.9. Found: C, 57.3; H, 6.98; N, 13.1%. IR: ν(BH) 2472 cm^{-1}; ν(NH) 3320 cm^{-1}. ^{1}H NMR (C_6D_6): δ 5.77 t, 5.98 t, 6.68 d, 7.54 d, 7.56 d, 8.14 d ($B(C_3\mathit{H}_3N_2)_3$); 6.94 t, 7.01 t, 7.08 t, 7.86 d ($HN{=}C(C_6\mathit{H}_4)(C_6\mathit{H}_5)$); 9.79 (s, br, $\mathit{H}N{=}$). $^{31}P\{^1H\}$ NMR: δ 80.9 s. $^{13}C\{^1H\}$ NMR: δ 18.7, 19.2, 19.8, 20.1 (s, $P(CH(\mathit{C}H_3)_2)_2$); 21.0 (m, $P\mathit{C}H_2$); 24.7, 25.5 (m, $P(\mathit{C}H(CH_3)_2)_2$); 105.2, 104.4, 134.6, 136.0, 143.2, 146.2 (s, $B(C_3H_3N_2)_3$); 127.5, 128.4, 129.3, 129.5, 130.4 ($HN{=}C(\mathit{C}_6H_4)(\mathit{C}_6H_5)$; 138.9 (t, $J_{CP} = 12.4$ Hz, Ru*C*); 177.1 (s, $HN{=}\mathit{C}(C_6H_5)_2$).

Table 1
Summary of data for the crystal structure analysis of **2**

Formula	$C_{58}H_{71}B_2N_7P_2Ru$
Formula weight	1050.88
Crystal size (mm)	0.20 × 0.12 × 0.40
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
Cell parameters	
a (Å)	14.180(4)
b (Å)	14.936(4)
c (Å)	13.471(5)
α (°)	101.76(3)
β (°)	91.88(3)
γ (°)	78.29(2)
V (Å^3)	2735(3)
Z	2
ρ_{calc} (g cm^{-3})	1.276
λ (Mo Kα) (Å)	0.71069
μ (Mo Kα) (cm^{-1})	3.80
F(000)	1104
Transmission factors	0.93–1.00 (ψ-scan method)
Scan speed (ω) (° min^{-1})	4.0
2θ interval (°)	$5.0 < 2\theta < 50.1$
Measured reflections	8649
Unique reflections	8325 [$R_{int} = 0.045$]
Observed reflections [$I > 3\sigma(I)$]	4804
Parameters	631
Reflection/parameter ratio	7.61
R [a]	0.048
R_w ($w = \sigma F^{-2}$) [b]	0.054
Maximum Δ/σ in final cycle	0.82
Goodness-of-fit	1.38

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

2.6. Preparation of [TpRu(σ-η^1-C_6H_5)(PEt_3)$_2$] (**6**)

A procedure analogous to that used for the preparation of **5** was used, starting from the imine adduct **2**. Yield: 60%. *Anal.* Calc. for $C_{27}H_{45}N_6BP_2Ru$: C, 51.7; H, 7.18; N, 13.4. Found: C, 51.5; H, 6.98; N, 13.4%. IR: ν(BH) 2464 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.66 (m, $PCH_2C\mathit{H}_3$), 1.73 (m, $PC\mathit{H}_2CH_3$); 5.80 t, 5.90 t, 7.47 d, 7.51 d, 8.20 br ($B(C_3\mathit{H}_3N_2)_3$); 7.29 t, 7.27 t, 8.09 br ($RuC_6\mathit{H}_5$). $^{31}P\{^1H\}$ NMR: δ 23.3 s. $^{13}C\{^1H\}$ NMR: δ 8.0 (s, $P(CH_2\mathit{C}H_3)_3$); 18.6 (t, $J_{CP} = 12$ Hz, $P(\mathit{C}H_2CH_3)_3$); 105.2, 105.3, 136.2, 137.1, 144.7, 147.7 (s, $B(\mathit{C}_3H_3N_2)_3$); 122.4, 126.4, 128.3 (s, C_6H_5), 132.2 (t, $J_{CP} = 9.6$ Hz, Ru*C*).

2.7. Experimental for the X-ray structure determination of compound **2**

A crystal suitable for X-ray diffraction analysis was mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer ($T = 290$ K, Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix were determined by least-squares fittings from the settings of 25 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 1. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standard reflections every 100 measurements. Decay and absorption corrections were also applied. Reflections having $I > 3\sigma(I)$ were used for structure refinement. 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 [16] software system and ORTEP [17] for plotting. The structure was solved by the Patterson method, and refined anisotropically by full-matrix least-squares methods for all non-hydrogen atoms. The hydrogen

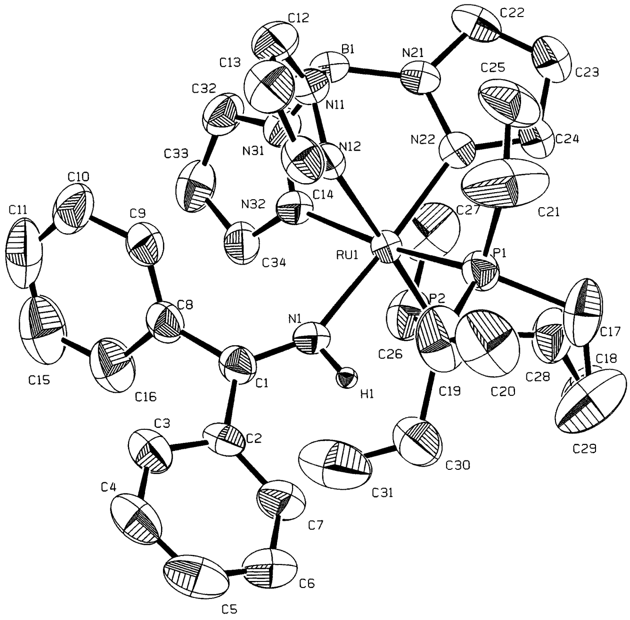


Fig. 1. ORTEP drawing of the complex cation [TpRu(HN=CPh$_2$)(PEt$_3$)$_2$]$^+$ in complex **2** with 50% probability thermal ellipsoids. Hydrogen atoms, except that on the nitrogen atom of the imine ligand, are omitted.

Table 2
Selected bond distances (Å) and angles (°) for [TpRu(HN=CPh$_2$)(PEt$_3$)$_2$][BPh$_4$]

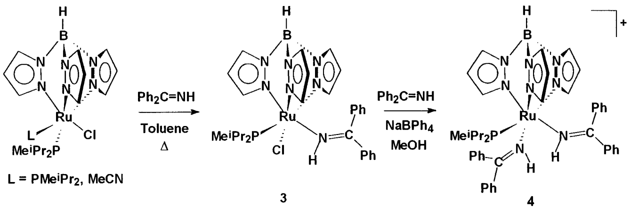
Ru(1)–P(1)	2.364(2)	Ru(1)–N(32)	2.140(5)
Ru(1)–P(2)	2.366(2)	N(1)–C(1)	1.309(7)
Ru(1)–N(1)	2.095(5)	N(1)–H(1)	0.9503
Ru(1)–N(12)	2.152(5)	C(1)–C(2)	1.472(9)
Ru(1)–N(22)	2.091(5)	C(1)–C(8)	1.485(9)
P(1)–Ru(1)–P(2)	99.28(7)	N(1)–Ru(1)–N(32)	92.3(2)
P(1)–Ru(1)–N(1)	89.5(2)	N(12)–Ru(1)–N(22)	86.5(2)
P(1)–Ru(1)–N(12)	87.4(2)	N(12)–Ru(1)–N(32)	83.2(2)
P(1)–Ru(1)–N(22)	90.1(2)	N(22)–Ru(1)–N(32)	87.5(2)
P(1)–Ru(1)–N(32)	170.4(2)	Ru(1)–N(1)–C(1)	147.2(5)
P(2)–Ru(1)–N(1)	92.3(1)	Ru(1)–N(1)–H(1)	106.3759
P(2)–Ru(1)–N(12)	173.0(2)	C(1)–N(1)–H(1)	106.4386
P(2)–Ru(1)–N(22)	91.4(2)	N(1)–C(1)–C(2)	119.9(6)
P(2)–Ru(1)–N(32)	90.1(2)	N(1)–C(1)–C(8)	122.4(6)
N(1)–Ru(1)–N(12)	89.8(2)	C(2)–C(1)–C(8)	117.7(6)
N(1)–Ru(1)–N(22)	176.3(2)		

atoms were included at idealized positions and not refined. Maximum and minimum peaks in the final difference Fourier maps were +0.80 and −0.41 e Å^{-3}.

3. Results and discussion

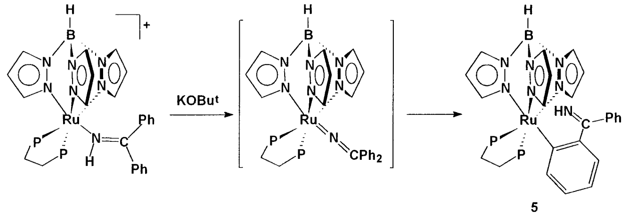
The complexes [TpRuCl(dippe)] and [TpRuCl(PEt$_3$)$_2$] react smoothly with benzophenone imine and NaBPh$_4$ in warm MeOH affording the corresponding mononuclear cationic imine complexes [TpRu(HN=CPh$_2$)(dippe)][BPh$_4$] (**1**) and [TpRu(HN=CPh$_2$)(PEt$_3$)$_2$][BPh$_4$] (**2**). These products are yellow crystalline solids which in their IR spectra display one medium band near 3300 cm^{-1}, attributable to ν(NH) in the imine ligand. The imine proton appears in the ^{1}H NMR spectra as one broad signal at approximately 10.30 ppm, whereas many resonances are observed in the aromatic region. Signals for the phenyl protons of the benzophenone imine ligand, six separate resonances for the pyrazole protons of the Tp group, as well as the tetraphenylborate protons all appear in the range 5.5–8.0 ppm, making this part of the ^{1}H NMR spectrum rather complicated. The ^{31}P{^{1}H} NMR spectra consists of one sharp singlet for both **1** and **2**. We have observed that the benzophenone imine is lost readily in solution. It appears that a rapid dissociation equilibrium occurs which leads to the formation of variable amounts of free imine plus other species. These species have been identified in some instances as solvent adducts, e.g. [TpRu(Me$_2$CO)(dippe)]$^+$, which had been described previously [11]. This behavior has been observed in other imine complexes of ruthenium, as in the case of [RuHCl(CO)(HN=CPh$_2$)(P^{i}Pr$_3$)$_2$] [18], and hence in all further operations for the purification of **1** and **2**, an excess of free imine was added to the liquor in order to prevent decomposition by imine ligand dissociation. Thus, single crystals of **2** suitable for X-ray structure analysis were obtained by recrystallization of the crude product from dichloromethane–petroleum ether containing free benzophenone imine. The crystal structure of compound **2** was determined. An ORTEP view of the complex cation is shown in Fig. 1. Relevant bond lengths and angles are listed in Table 2. The coordination around ruthenium is distorted octahedral, with phosphines in a *cisoid* arrangement, with a P(1)–Ru(1)–P(2) angle of 99.28(7)°. The Ru(1)–N(1) and N(1)–C(1) bond lengths of 2.095(5) and 1.309(7) Å correspond to single Ru–N and double C=N bonds, respectively. The Ru(1)–N(1) separation is slightly shorter than that found in [RuCl$_2$(HN=CPh$_2$)(CO)(PMe^{i}Pr$_2$)$_2$] (2.144(5) Å) [10], being indicative of a stronger metal–imine interaction in the case of **2**. The angles around C(2) indicate a sp^2 hybridization as expected. The phenyl rings of the imine ligand are oriented in a way that their planes form 72.73°. A similar value of 69.44° has been found for the angle between the planes defined by the atoms Ru(1), N(1), N(12), N(22) and P(2) and the atoms N(1), C(1), C(2) and C(8) of the benzophenone imine ligand. All the dimensions in the phosphine and Tp groups, as well as in the [BPh$_4$]$^-$ anion are in the normal range.

All attempts carried out to prepare the cationic imine complex [TpRu(HN=CPh$_2$)(PMe^{i}Pr$_2$)$_2$][BPh$_4$] following the same procedure used for the synthesis of **1** and **2** led to the formation of mixtures. Using ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, we monitored the reaction of the dinitrogen complex $[TpRu(N_2)(PMe^iPr_2)_2][BPh_4]$ [12] with an excess of benzophenone imine. Rapid substitution of dinitrogen and subsequent formation in situ of the expected complex $[TpRu(HN{=}CPh_2)(PMe^iPr_2)_2][BPh_4]$ was observed, but shortly afterwards, the $^{31}P\{^1H\}$ resonance attributed to this species disappeared and were replaced by two new signals, one of which was due to the free PMe^iPr_2, and the other one corresponding to a new species, which contains apparently only one phospine ligand bound to the metal. The lability of PMe^iPr_2 in bis(methyldiisopropylphosphine) derivatives is well established, and this has allowed us to access a range of neutral compounds resulting from the substitution of one phosphine by neutral donors [12,14]. Thus, the reaction of $[TpRuCl(PMe^iPr_2)_2]$, or even more conveniently $[TpRuCl(PMe^iPr_2)(MeCN)]$ with benzophenone imine in toluene at 70°C led to the substitution of either one phosphine or MeCN and the formation of the red neutral imine derivative $[TpRuCl(HN{=}CPh_2)(PMe^iPr_2)]$ (**3**), which was isolated upon concentration and addition of petroleum ether. Benzophenone imine is readily released from **3**, and hence free imine must be added in order to prevent dissociation and decomposition. Compound **3** reacts with further benzophenone imine in MeOH in the presence of $NaBPh_4$ affording the cationic bis(imine) complex $[TpRu(HN{=}CPh_2)_2(PMe^iPr_2)][BPh_4]$ (**4**), which was identified as the final compound formed in the reaction between $[TpRu(N_2)(PMe^iPr_2)_2][BPh_4]$ and $HN{=}CPh_2$.

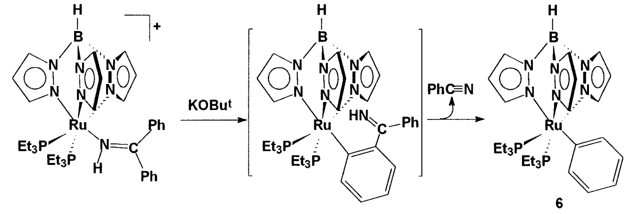


Both **3** and **4** exhibit, in their IR spectra, bands attributable to ν(NH) as expected. The NH proton appears in the ^1H NMR spectra as one broad signal at 13.08 ppm for **3** and 11.01 ppm for **4**. Apparently, this resonance shifts to lower fields for a neutral complex, by comparison with the values found in cationic complexes. Complex **3** is a red–orange solid, very soluble in most common organic solvents, where it dissociates benzophenone imine easily, as seen above. Nine separate pyrazole proton and carbon resonances are observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra for the Tp ligand, resulting from the chemical and magnetic inequivalence of the three pyrazole rings, a feature that it has been observed previously for other $[TpRuCl(PMe^iPr_2)(L)]$ derivatives [12,14]. Compound **4** is a yellow–orange, crystalline material, which constitutes a rare example of a bis(imine) derivative. This sort of compound may play an important role as a catalyst for processes such as imine metathesis, or the coupling of imines with alkynes and olefins. These possibilities are currently under study.

In contrast with the well-documented chemistry of vinylidene complexes [19], little is known about azavinylidene complexes, formally related to the former, containing one nitrogen atom at the α-position of the unsaturated ligand [18]. Azavinylidene complexes of Os and Ir have been prepared by the deprotonation of the corresponding imine adducts, e.g. $[(\eta^6\text{-}C_6H_6)\text{-}Os{=}N{=}CPh_2(PMe^tBu_2)][PF_6]$ [20]. Azavinylidene complexes of ruthenium, both mononuclear [21] and polinuclear [22], are also known. In an attempt to generate neutral azavinylidene derivatives, we carried out the deprotonation of **2** and **3** using $KOBu^t$. Unexpectedly, no azavinylidene complexes were obtained. In both cases, *ortho*-metalation of one of the phenyl rings of the benzophenone imine took place, giving rise to species containing a direct Ru–C bond. Thus, the product of the reaction of **1** with $KOBu^t$ in tetrahydrofuran has been identified as $[TpRu\{\sigma\text{-}\eta^1\text{-}C_6H_4C(Ph){=}NH\}(dippe)]$ (**5**), in which the NH group of the imine is not coordinated to ruthenium.



In the case of the deprotonation of **2**, the reaction goes further apparently, and the final product is the σ-aryl derivative $[TpRu(\sigma\text{-}\eta^1\text{-}C_6H_5)(dippe)]$ (**6**), with no evidence for the presence of the imine group. This de-arylation reaction is feasible assuming that benzonitrile is released spontaneously from a species analogous to **5**.



However, we have been unable to detect benzonitrile, since it is lost during the work-up of the reaction mixture, so this proposal must be taken with due caution. It seems that the imine proton is abstracted by $KOBu^t$ for both **1** and **2**, giving rise to an intermediate azavinylidene complex, which rearranges possibly yielding *ortho*-metalated derivatives, a reaction which has precedents in ruthenium and osmium chemistry [8,18]. The de-arylation of the benzophenone imine leading to the phenyl derivative **6** resembles the recently reported decarbonylation of alcohols by [TpRuH(MeCN)-(PPh_3)], a process which yields alkyl- or aryl-TpRu carbonyl complexes of the type [TpRuR(CO)(PPh_3)] [23]. Both **5** and **6** display one triplet resonance in their $^{13}C\{^1H\}$ NMR spectra attributable to the metal-bound carbon atom of the phenyl ring. The ^1H NMR spectrum of **5** displays one broad resonance at 9.79 ppm due to the NH proton, consistent with the presence of a weak ν(NH) band at 3320 cm^{-1} in the IR spectrum. At variance with this, the ^1H NMR spectrum of **6** is much simpler in the aromatic region, showing no evidence for the presence of NH protons. We have also tried to deprotonate the bis(imine) complex **4**. A red solid has been obtained, which also shows evidence for *ortho*-metalation, being apparently binuclear, as inferred from NMR spectroscopy. The full characterization of this compound is still underway and will be reported in due course. It appears clear from this study that deprotonation of imine adducts is a complex process which does not always lead to stable azavinylidene derivatives.

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