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Oxidative addition of O_2, Cl_2, NO, NO^+ and H_2 to $[Ru(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CH_2PPh_2)]^+$: X-ray structures of $[Ru(Cl)_2(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CH_2PPh_2)]^+$ and $[Ru(NO)(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CH_2PPh_2)]^{2+}$

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Abstract

Treatment of $Ru(\eta^5\text{-}C_5Me_5)(dppe)Cl$ (**1**) ($dppe=Ph_2PCH_2CH_2PPh_2$) with Ag^+ (as the PF_6^- or $CF_3SO_3^-$ salt) in CH_3NO_2 as the solvent yields the 16-electron complex $[Ru(\eta^5\text{-}C_5Me_5)(dppe)]^+$ (**2**) in quantitative yield. Complex **2** reacts with O_2, Cl_2, NO, NO^+ and H_2 to form the cationic Ru(IV) complexes $[Ru(\eta^2\text{-}O_2)(\eta^5\text{-}C_5Me_5)(dppe)]^+$ (**3**), $[Ru(Cl)_2(\eta^5\text{-}C_5Me_5)(dppe)]^+$ (**4**), $[Ru(NO)(\eta^5\text{-}C_5Me_5)(dppe)]^{2+}$ (**5**) and $[Ru(H)_2(\eta^5\text{-}C_5Me_5)(dppe)]^+$ (**6**) in good yields. The crystal structures of **4b** ($CF_3SO_3^-$ salt) and **5b** ($CF_3SO_3^-$ salt) have been determined by X-ray diffraction techniques. **4b** crystallizes in the triclinic space group $P\bar{1}$ (No. 2), with $a=12.215(4)$, $b=12.593(5)$, $c=14.422(4)$ Å, $\alpha=76.45(2)$, $\beta=79.83(2)$, $\gamma=84.64(2)°$, $V=2119.7(12)$ Å^3, $Z=2$. The structure was refined to $R(F)=0.0418$ ($F\geq 4\sigma F$). **5b** crystallizes in the monoclinic space group $P2_1/n$, with $a=12.679(4)$, $b=12.269(5)$, $c=27.658(9)$ Å, $\beta=90.36(1)°$, $V=4302(3)$ Å^3, $Z=4$. The structure was refined to $R(F)=0.0511$ ($F\geq 4\sigma F$).

Keywords: Crystal structures; Oxidative additions; Ruthenium complexes; Pentamethylcyclopentadienyl complexes; Nitrosyl complexes

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1. Introduction

In a recent communication [1] we reported on the facile irreversible binding of dioxygen and other gases, namely, Cl_2, NO and H_2, to the coordinatively unsaturated half-sandwich Ru(II) complex $[Ru(\eta^5\text{-}C_5Me_5)(dppe)]^+$ ($dppe=Ph_2PCH_2CH_2PPh_2$) in CH_3NO_2 as the solvent. Of these complexes, only the side-on bonded peroxide complex $[Ru(\eta^2\text{-}O_2)(\eta^5\text{-}C_5Me_5)(dppe)]PF_6$ was described in more detail which included an X-ray crystal structure determination.

Herein we give a full account of the preparation and characterization of $[Ru(\eta^2\text{-}O_2)(\eta^5\text{-}C_5Me_5)(dppe)]PF_6$ and the other oxidative addition products. Furthermore, we present the X-ray crystal structures of the Ru(IV) complexes $[Ru(Cl)_2(\eta^5\text{-}C_5Me_5)(dppe)]CF_3SO_3$ and $[Ru(NO)(\eta^5\text{-}C_5Me_5)(dppe)](CF_3SO_3)_2$.

2. Experimental

Manipulations were performed under an inert atmosphere of purified nitrogen by using standard Schlenk techniques and/or a glove box. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [2]. In order to remove propionitrile, nitromethane was purified by crystallization [3] followed by fractional distillation. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. IR spectra were obtained on a Mattson RS1 FT-IR spectrometer. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer and were referenced to $SiMe_4$ and PPh_3, respectively. Microanalyses were conducted by Microanalytical Laboratories, University of Vienna, Austria.

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Ru(η^5-C_5Me_5)(dppe)Cl (**1**) was prepared by a published procedure [4].

2.1. Preparation of solutions of [Ru(η^5-C_5Me_5)(dppe)]$^+$ (2)

A solution of **1** (500 mg, 0.782 mmol) in nitromethane (5 ml) was treated with Ag^+ (1 equiv.), introduced as PF_6^- or $CF_3SO_3^-$ salts, whereupon an immediate color change from orange to dark red was seen. The mixture was stirred for 1 h and the AgCl formed was allowed to settle and was removed by filtration. The reaction is quantitative as followed by ^{1}H NMR spectroscopy. ^{1}H NMR (250.13 MHz, δ, CD_3NO_2, 20 °C): 7.80–7.30 (m, 20H), 3.13 (d, 4H), 1.36 (s, 15H). ^{13}C{^{1}H} NMR (62.86 MHz, δ, CD_3NO_2, 20 °C): 133.7–130.0 (C_6H_5), 94.6 (C_5Me_5), 32.0 (t, PCH_2CH_2P), 9.7 (C_5Me_5).

2.2. Synthesis of [Ru(η^2-O_2)(η^5-C_5Me_5)(dppe)]PF_6 (3)

A solution of **2** (as PF_6^- salt) was purged with air for 2 h, whereupon the color of the solution turned brown. On addition of anhydrous diethyl ether a brown precipitate of **3** was formed, which was collected on a glass frit, washed with anhydrous diethyl ether and dried under vacuum. Yield: 67%. *Anal.* Calc. for $C_{35}H_{39}F_6O_2P_3Ru$: C, 53.27; H, 4.84; P, 11.45. Found: C, 52.69; H, 4.72; P, 11.22%. ^{1}H NMR (250.13 MHz, δ, CD_3NO_2, 20 °C): 7.80–7.10 (m, 20H), 2.68 (d, 4H), 1.57 (t, 15H). ^{13}C{^{1}H} NMR (62.86 MHz, δ, CD_3NO_2, 20 °C): 139.0–134.2 (C_6H_5), 112.4 (C_5Me_5), 30.8 (t, PCH_2CH_2P), 13.2 (C_5Me_5). ^{31}P{^{1}H} NMR (101.26 MHz, δ versus PPh_3, CD_3NO_2, 20 °C): 75.62. IR (KBr pellet, cm^{-1}): 3064 (m), 2923 (m), 1482 (m), 1437 (s), 1190 (m), 1097 (s), 934 (m), 880 (m), 839 (s, PF_6^-), 753 (s), 698 (s), 557 (s, PF_6^-), 529 (s).

2.3. Synthesis of [Ru(Cl)$_2$(η^5-C_5Me_5)(dppe)]PF_6 (4a)

A solution of **2** (as PF_6^- salt, 0.782 mmol) was purged with Cl_2 for 1 min. Addition of anhydrous diethyl ether afforded a red precipitate of **4a** which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 81%. *Anal.* Calc. for $C_{36}H_{39}Cl_2F_6P_3Ru$: C, 50.83; H, 4.62; P, 10.92. Found: C, 51.33; H, 4.50; P, 9.98%. ^{1}H NMR (250.13

Table 1
Crystal data and structure refinement [a] for [Ru(Cl)$_2$(η^5-C_5Me_5)(dppe)]·CF_3SO_3·$2CH_3NO_2$ (**4b**) and [Ru(NO)(η^5-C_5Me_5)(dppe)]·$2CF_3SO_3$·CH_3NO_2 (**5b**)

	4b	**5b**
Formula	$C_{39}H_{45}Cl_2F_3N_2O_7P_2RuS$	$C_{39}H_{42}F_6N_2O_9P_2RuS_2$
Formula weight	976.74	1023.88
Crystal size (mm)	0.3×0.4×0.5	0.30×0.50×0.66
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	12.215(4)	12.679(4)
b (Å)	12.593(5)	12.269(5)
c (Å)	14.422(4)	27.658(9)
α (°)	76.45(2)	90
β (°)	79.83(2)	90.36(1)
γ (°)	84.64(2)	90
V (Å^3)	2119.7(12)	4302(3)
Z	2	4
Density (calc.) (g cm^{-3})	1.530	1.581
T (K)	297	297
μ (mm^{-1})	0.684	0.617
Diffractometer	Philips PW1100	Philips PW1100
Radiation	Mo Kα	Mo Kα
Scan type	θ–2θ	ω
θ_{max} (°)	25	25
Ranges for h, k, l	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $0 \leq l \leq 17$	$-15 \leq h \leq 15$, $0 \leq k \leq 14$, $-32 \leq l \leq 32$
Absorption correction (transmission)	none	analytical (0.85–0.93)
No. measured reflections	7484	13923
No. unique reflections	7484	7592
No. reflections above $4\sigma F$	6336	5320
No. parameters	520	557
$R(F)$ ($F>4\sigma F$)	0.0418	0.0511
$R(F)$ (all data)	0.0535	0.0764
$wR(F^2)$ (all data)	0.1034	0.1517
$\Delta\rho$ (max./min.) (e Å^{-3})	0.61/−0.59	0.86/−0.60

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

MHz, δ, CD_3NO_2, 20 °C): 7.80–6.80 (m, 20H), 3.46 (b, 2H), 3.21 (b, 2H), 1.32 (t, 15H). $^{13}C\{^1H\}$ NMR (62.86 MHz, δ, CD_3NO_2, 20 °C): 136.0–128.0 (C_6H_5), 113.5 (C_5Me_5), 26.3 (t, PCH_2CH_2P), 9.7 (C_5Me_5). $^{31}P\{^1H\}$ NMR (101.26 MHz, δ versus PPh_3, CD_3NO_2, 20 °C): 60.66.

$[Ru(Cl)_2(\eta^5\text{-}C_5Me_5)(dppe)]CF_3SO_3$ (**4b**) was prepared in analogous fashion utilizing the $CF_3SO_3^-$ salt of **2** as starting material. Crystals of **4b** were grown by vapor diffusion of diethyl ether into a nitromethane solution of the complex.

2.4. Synthesis of $[Ru(NO)(\eta^5\text{-}C_5Me_5)(dppe)](PF_6)_2$ (5a)

(a) Passing NO through a solution of **2** (as PF_6^- salt) for 15 min gave on addition of anhydrous diethyl ether an orange precipitate of the nitrosyl complex **5a**, which was collected on a glass frit, washed with anhydrous diethyl ether and dried under vacuum. Yield: 44%. (b) Addition of $NOPF_6$ to a stirred solution of **1** (500 mg, 0.782 mmol) in CH_2Cl_2 afforded an orange precipitate of **5a**, which was collected on a glass frit, washed with anhydrous diethyl ether and dried under vacuum. Yield: 87%. *Anal.* Calc. for $C_{36}H_{39}F_{12}NOP_4Ru$: C, 45.29; H, 4.12; N, 1.47; P, 12.98. Found: C, 44.10; H, 3.56; N, 1.46; P, 12.75%. ^1H NMR (250.13 MHz, δ, CD_3NO_2, 20 °C): 7.80–7.30 (m, 20H), 3.57 (d, 4H), 1.84 (s, 15H). $^{13}C\{^1H\}$ NMR (62.86 MHz, δ, CD_3NO_2, 20 °C): 135.0–128.0 (C_6H_5), 115.5 (C_5Me_5), 30.0 (t, PCH_2CH_2P), 10.2 (C_5Me_5). $^{31}P\{^1H\}$ NMR (101.26 MHz, δ versus PPh_3, $[^2H_6]$acetone, 20 °C): 66.35. IR (KBr pellet, cm^{-1}): 1850 (s, ν(NO)).

$[Ru(NO)(\eta^5\text{-}C_5Me_5)(dppe)](CF_3SO_3)_2$ (**5b**) was prepared in analogous fashion utilizing the $CF_3SO_3^-$ salt of **2** as starting material. Crystals of **5b** were grown by vapor diffusion of diethyl ether into a nitromethane solution of the complex.

2.5. Synthesis of $[Ru(H)_2(\eta^5\text{-}C_5Me_5)(dppe)]CF_3SO_3$ (6)

A solution of **2** (as $CF_3SO_3^-$ salt) was purged with H_2 for 10 min. Complex **6** was precipitated with diethyl ether as a pale yellow solid, which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 38%. *Anal.* Calc. for $C_{37}H_{41}F_3O_3P_2SRu$: C, 56.55; H, 5.26; P, 7.38. Found: C, 56.08; H, 5.26; P, 7.31%. ^1H NMR (250.13 MHz, δ, CD_3NO_2, 20 °C): 7.70–7.50 (m, 20H), 2.43 (d, 4H), 1.71 (t, 15H), −8.58 (t, J(PH) = 28.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (62.86 MHz, δ, CD_3NO_2, 20 °C): 135.0–130.0 (C_6H_5), 101.2 (C_5Me_5), 33.5 (t, PCH_2CH_2P), 10.7 (C_5Me_5).

2.6. X-ray structure determination for 4b and 5b

Crystal data and experimental details are given in Table 1. The structures were solved with Patterson and Fourier methods [5], and were then refined against F^2 using program SHELXL93 [6]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions riding on the atoms to which they were bonded. Soft distance restraints (**4b**, **5b**) and site occupation factor refinement (**5b**) were used for the $CF_3SO_3^-$ anions and for the CH_3NO_2 molecules. Positional parameters are presented in Tables 2 and 3.

3. Results and discussion

3.1. Synthesis and spectroscopic data

Complex **1** reacts with silver salts of non-coordinating anions such as PF_6^- and $CF_3SO_3^-$ in the poorly coordinating solvent CH_3NO_2 at room temperature to afford the dark-red cationic 16-electron complex $[Ru(\eta^5\text{-}C_5Me_5)(dppe)]^+$ (**2**). Characterization of this complex, however, was possible only in solution by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy since attempts of isolation were unsuccessful. From this spectroscopic evidence, the same product was obtained independent of whether the inert atmosphere was N_2 or Ar. It can therefore be concluded that N_2 does not participate in the reaction. Noteworthily, a related 16-electron complex, $[Ru(\eta^5\text{-}C_5H_5)(cy_2PCH_2CH_2Pcy_2)]^+$ (cy = cyclohexyl), has been postulated recently [7].

On passing one of the gases O_2, Cl_2, NO or H_2 through solutions of **2**, complexes **3**–**6** are readily obtained after synthetic workup. The nitrosyl complex **5** is also available from reaction of complex **1** with $NOPF_6$ in CH_2Cl_2 as the solvent. Analogous dichloro and nitrosyl complexes of the $C_5H_5^-$ series with PR_3 (R = Me, Ph) as ancillary ligands, $[Ru(Cl)_2(\eta^5\text{-}C_5H_5)(PR_3)_2]PF_6$ and $[Ru(NO)(\eta^5\text{-}C_5H_5)(PR_3)_2](PF_6)_2$, have been reported previously [8]. In the case of the less basic and more bulky phosphine PPh_3, however, no isolable products were obtained [8]. This illustrates the increased stability of the Ru(IV) oxidation state when the stronger π-donor $C_5Me_5^-$ is used instead of parent $C_5H_5^-$. The straightforward formation of the dihydride complex **6** by direct reaction of H_2 with $[Ru(\eta^5\text{-}C_5Me_5)(dppe)]^+$ (**2**) is worth noting. Compounds of that type are commonly more difficult to obtain, for instance, by protonation of monohydride complexes $[Ru(H)(\eta^5\text{-}C_5Me_5)(L)_2]^+$ (L = various tertiary phosphine ligands) with strong acids [9,10]. It is interesting to note that the related complex $Ru(\eta^5\text{-}C_5H_5)((C_2F_5)_2PCH_2CH_2P(C_2F_5)_2)Cl$ in the presence of Ag^+ and H_2 does not yield a dihydride species but only the mono-hydride complex $Ru(H)(\eta^5\text{-}C_5H_5)((C_2F_5)_2PCH_2CH_2P(C_2F_5)_2)$ [11].

Compounds **3**–**6** are crystalline and air-stable solids characterized by a combination of elemental analyses, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In addition, complexes **3**–**5** were characterized by their $^{31}P\{^1H\}$ NMR and IR spectra. The ^1H NMR spectra of **3**–**6** all show the expected resonance for the $C_5Me_5^-$ ring appearing as a triplet due to coupling with ^{31}P in the range of 1.32–1.84 ppm. Likewise, the characteristic multiplet resonances assignable to the phosphine ligand are observed in the expected ranges. The resonance of

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for [Ru(Cl)$_2$(η^5-C$_5$Me$_5$)(dppe)]·CF$_3$SO$_3$·2CH$_3$NO$_2$ (**4b**)

	x	y	z	U_{eq} [a]
Ru	0.43453(2)	0.22111(2)	0.17873(2)	34(1)
Cl(1)	0.53192(8)	0.10819(8)	0.07458(7)	51(1)
Cl(2)	0.45252(8)	0.35076(8)	0.02727(6)	48(1)
C(1)	0.6066(3)	0.2439(3)	0.2036(3)	48(1)
C(2)	0.5630(3)	0.1483(3)	0.2712(3)	46(1)
C(3)	0.4695(3)	0.1838(3)	0.3324(3)	43(1)
C(4)	0.4559(3)	0.3004(3)	0.3045(3)	43(1)
C(5)	0.5422(3)	0.3373(3)	0.2258(3)	45(1)
C(6)	0.7093(3)	0.2485(4)	0.1302(4)	68(1)
C(7)	0.6183(4)	0.0362(4)	0.2839(4)	64(1)
C(8)	0.4137(4)	0.1183(3)	0.4267(3)	57(1)
C(9)	0.3869(4)	0.3698(4)	0.3662(3)	57(1)
C(10)	0.5679(4)	0.4528(3)	0.1812(3)	62(1)
P(1)	0.32195(8)	0.07144(7)	0.20837(7)	38(1)
P(2)	0.24904(7)	0.30457(7)	0.18607(6)	35(1)
C(11)	0.3778(3)	−0.0670(3)	0.2565(3)	46(1)
C(12)	0.4399(3)	−0.1256(3)	0.1927(3)	54(1)
C(13)	0.4872(4)	−0.2278(4)	0.2261(4)	68(1)
C(14)	0.4708(4)	−0.2748(4)	0.3230(4)	77(2)
C(15)	0.4079(4)	−0.2200(4)	0.3869(4)	71(1)
C(16)	0.3605(4)	−0.1159(3)	0.3546(3)	57(1)
C(17)	0.2637(3)	0.0506(3)	0.1061(3)	42(1)
C(18)	0.2885(3)	0.1138(3)	0.0137(3)	45(1)
C(19)	0.2371(3)	0.0956(4)	−0.0591(3)	58(1)
C(20)	0.1621(4)	0.0158(4)	−0.0392(4)	66(1)
C(21)	0.1371(4)	−0.0477(4)	0.0531(4)	67(1)
C(22)	0.1880(3)	−0.0307(3)	0.1256(3)	55(1)
C(23)	0.2284(3)	0.4424(3)	0.2074(3)	41(1)
C(24)	0.2913(3)	0.5273(3)	0.1502(3)	49(1)
C(25)	0.2721(4)	0.6324(3)	0.1660(4)	61(1)
C(26)	0.1905(4)	0.6521(4)	0.2393(4)	71(1)
C(27)	0.1272(4)	0.5704(4)	0.2955(4)	65(1)
C(28)	0.1447(3)	0.4657(3)	0.2798(3)	53(1)
C(29)	0.1661(3)	0.3189(3)	0.0887(3)	42(1)
C(30)	0.1868(3)	0.3995(4)	0.0046(3)	55(1)
C(31)	0.1203(4)	0.4154(5)	−0.0651(4)	74(1)
C(32)	0.0311(4)	0.3513(5)	−0.0524(4)	75(1)
C(33)	0.0093(3)	0.2719(4)	0.0301(4)	64(1)
C(34)	0.0759(3)	0.2554(3)	0.1003(3)	51(1)
C(35)	0.1978(3)	0.0953(3)	0.2962(3)	47(1)
C(36)	0.1700(3)	0.2184(3)	0.2915(3)	43(1)
C(37)	0.1421(10)	0.2066(10)	0.6688(7)	176(5)
F(1)	0.0950(6)	0.2670(6)	0.7248(4)	228(4)
F(2)	0.1388(10)	0.1018(9)	0.7281(4)	310(7)
F(3)	0.2454(6)	0.2116(9)	0.6478(7)	252(5)
S	0.0721(2)	0.2045(2)	0.5744(1)	103(1)
O(1)	0.1373(4)	0.1272(5)	0.5265(3)	132(2)
O(2)	0.0739(6)	0.3127(5)	0.5220(4)	153(2)
O(3)	−0.0369(5)	0.1697(6)	0.6217(5)	172(3)
C(38)	0.8985(8)	0.1234(9)	0.4425(7)	173(4)
N(1)	0.8316(7)	0.1677(10)	0.3749(6)	172(4)
O(4)	0.7306(6)	0.1858(9)	0.3983(6)	232(5)
O(5)	0.8776(8)	0.1886(21)	0.2944(6)	525(19)
C(39)	0.8114(9)	0.4436(8)	0.4712(8)	176(4)
N(2)	0.7472(16)	0.4489(10)	0.3983(8)	290(10)
O(6)	0.6580(13)	0.4795(12)	0.4190(13)	322(10)
O(7)	0.8009(19)	0.4280(22)	0.3315(11)	521(20)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j (a_i a_j)$.

the hydride ligands of complex **6** appear as a sharp triplet at −8.58 ppm because of coupling to two equivalent phosphorus nuclei (^2J(HP) = 28.3 Hz). Therefore, under the reaction conditions employed, it appears that a classical dihydride

Table 3
Atomic coordinates and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for [Ru(NO)(η^5-C$_5$Me$_5$)(dppe)]·2CF$_3$SO$_3$·CH$_3$NO$_2$ (**5b**)

	x	y	z	U_{eq} [a]
Ru	0.14227(3)	0.24434(3)	0.37928(1)	43(1)
N(1)	0.1895(3)	0.3422(3)	0.3389(2)	61(1)
O(1)	0.2124(4)	0.4108(4)	0.3132(2)	111(2)
C(1)	0.0191(4)	0.3591(4)	0.4075(2)	58(1)
C(2)	0.0737(4)	0.3145(4)	0.4470(2)	55(1)
C(3)	0.0533(4)	0.1997(4)	0.4479(2)	54(1)
C(4)	−0.0152(4)	0.1755(4)	0.4089(2)	57(1)
C(5)	−0.0351(4)	0.2730(4)	0.3831(2)	59(1)
C(6)	0.0113(6)	0.4772(4)	0.3941(2)	89(2)
C(7)	0.1261(5)	0.3794(5)	0.4867(2)	83(2)
C(8)	0.0815(5)	0.1242(5)	0.4885(2)	78(2)
C(9)	−0.0741(5)	0.0707(6)	0.4018(2)	98(2)
C(10)	−0.1133(5)	0.2890(7)	0.3429(2)	98(2)
P(1)	0.31543(9)	0.19198(10)	0.40782(5)	51(1)
P(2)	0.17819(10)	0.10919(10)	0.31922(4)	53(1)
C(11)	0.3466(4)	0.1606(4)	0.4704(2)	62(1)
C(12)	0.3840(5)	0.2407(5)	0.5009(2)	88(2)
C(13)	0.4099(8)	0.2134(8)	0.5480(3)	131(3)
C(14)	0.3966(7)	0.1119(8)	0.5654(3)	126(3)
C(15)	0.3607(6)	0.0314(7)	0.5358(3)	108(2)
C(16)	0.3345(5)	0.0553(5)	0.4876(2)	84(2)
C(17)	0.4056(4)	0.3007(4)	0.3912(2)	55(1)
C(18)	0.3802(4)	0.4078(4)	0.4036(2)	66(1)
C(19)	0.4484(5)	0.4914(5)	0.3914(2)	86(2)
C(20)	0.5373(5)	0.4696(6)	0.3661(2)	93(2)
C(21)	0.5620(5)	0.3655(6)	0.3527(2)	86(2)
C(22)	0.4978(4)	0.2794(5)	0.3650(2)	66(1)
C(23)	0.1125(4)	−0.0204(4)	0.3202(2)	57(1)
C(24)	0.0627(5)	−0.0619(5)	0.2795(2)	78(2)
C(25)	0.0146(6)	−0.1634(6)	0.2809(3)	100(2)
C(26)	0.0199(7)	−0.2236(5)	0.3209(3)	104(2)
C(27)	0.0659(5)	−0.1852(5)	0.3625(2)	91(2)
C(28)	0.1131(4)	−0.0833(4)	0.3615(2)	72(2)
C(29)	0.1576(5)	0.1641(4)	0.2592(2)	69(1)
C(30)	0.0713(7)	0.2235(7)	0.2486(2)	120(3)
C(31)	0.0591(9)	0.2656(7)	0.2016(3)	133(4)
C(32)	0.1262(10)	0.2455(6)	0.1677(2)	111(3)
C(33)	0.2119(8)	0.1853(7)	0.1771(3)	114(3)
C(34)	0.2312(6)	0.1455(6)	0.2229(2)	94(2)
C(35)	0.3552(4)	0.0707(4)	0.3747(2)	71(2)
C(36)	0.3198(4)	0.0785(5)	0.3229(2)	73(2)
C(37)	0.2044(6)	0.1749(8)	−0.0213(3)	100(2)
F(1)	0.1802(10)	0.2454(5)	−0.0514(3)	271(6)
F(2)	0.2590(6)	0.1034(6)	−0.0463(2)	200(3)
F(3)	0.1258(6)	0.1204(8)	−0.0114(2)	230(4)
S(1)	0.27545(15)	0.22318(17)	0.02921(6)	88(1)
O(2)	0.2818(7)	0.1325(5)	0.0600(2)	161(3)
O(3)	0.2054(8)	0.2958(6)	0.0511(2)	197(4)
O(4)	0.3536(9)	0.2673(15)	0.0122(3)	396(12)
C(38)	0.7252(9)	0.0076(14)	0.2590(5)	308(14)
F(4)	0.8024(5)	0.0285(8)	0.2837(4)	298(6)
F(5)	0.7232(8)	−0.1065(8)	0.2546(4)	306(7)
F(6)	0.7446(8)	0.0355(10)	0.2128(4)	332(8)
S(2)	0.60483(15)	0.04291(17)	0.27398(7)	99(1)
O(5)	0.5865(5)	0.0094(5)	0.3203(2)	141(2)
O(6)	0.6384(9)	0.1658(5)	0.2748(3)	253(5)
O(7)	0.5325(5)	0.0196(7)	0.2380(2)	167(3)
C(39) [b]	0.2532(16)	0.2337(17)	0.6649(7)	146(8)
N(2) [b]	0.2113(12)	0.2850(17)	0.6210(5)	111(5)
O(8) [b]	0.1569(14)	0.2359(19)	0.5961(6)	205(10)
O(9) [b]	0.2379(17)	0.3697(17)	0.6104(7)	197(9)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j (a_i a_j)$.

[b] Nitromethane, refined site occupation factor 0.49(1).

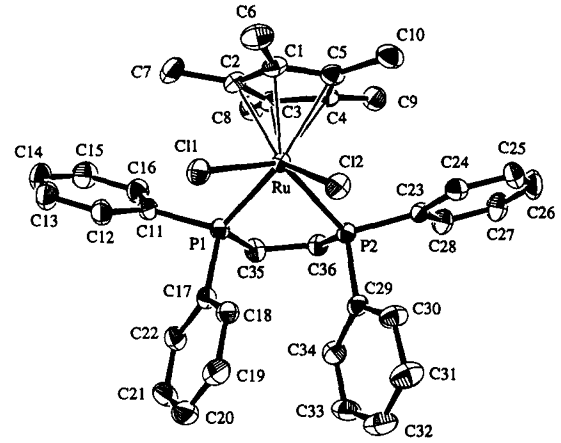

Fig. 1. ORTEP plot (30% ellipsoids) of $[Ru(Cl)_2(\eta^5\text{-}C_5Me_5)(dppe)]\text{-}CF_3SO_3 \cdot 2CH_3NO_2$ (**4b**) ($CF_3SO_3^-$ and CH_3NO_2 omitted for clarity).

rather than a dihydrogen complex is dealt with. This is supported by the fact that for the analogous dihydride complexes $[Ru(H)_2(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2PPh_2)]^+$ and $[Ru(H)_2(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CH_2CH_2PPh_2)]^+$ the proton resonances of the hydride ligands are also found as apparent triplets at −6.09 (^2J(HP) = 28.8 Hz) and −8.76 ppm (^2J(HP) = 29.0 Hz), respectively, whereas the corresponding dihydrogen complexes exhibit broad peaks at −6.80 and −8.80 ppm, respectively [10].

Table 4
Selected bond lengths[a] (Å) and angles (°) for $[Ru(Cl)_2(\eta^5\text{-}C_5Me_5)\text{-}(dppe)] \cdot CF_3SO_3 \cdot 2CH_3NO_2$ (**4b**) and $[Ru(NO)(\eta^5\text{-}C_5Me_5)(dppe)] \cdot 2CF_3SO_3 \cdot CH_3NO_2$ (**5b**)

	4b	**5b**
Ru–Cl(1)	2.397(1)	
Ru–Cl(2)	2.390(1)	
Ru–N(1)		1.748(4)
Ru–P(1)	2.351(1)	2.415(1)
Ru–P(2)	2.403(1)	2.393(1)
Ru–C(1)	2.249(4)	2.247(4)
Ru–C(2)	2.231(4)	2.243(4)
Ru–C(3)	2.264(4)	2.280(4)
Ru–C(4)	2.327(4)	2.322(4)
Ru–C(5)	2.339(4)	2.279(5)
$\langle Ru–C_{cp} \rangle$	2.282(4)	2.274(4)
$\langle C_{cp}–C_{cp} \rangle$	1.427(5)	1.418(7)
$\langle C_{cp}–C_{Me} \rangle$	1.492(5)	1.500(7)
$\langle C_{Ph}–C_{Ph} \rangle$	1.380(6)	1.372(9)
$\langle P–C \rangle$	1.832(4)	1.816(5)
N(1)–O(1)		1.141(5)
Cl(1)–Ru–Cl(2)	79.86(4)	
Cl(1)–Ru–P(1)	76.13(4)	
Cl(1)–Ru–P(2)	130.15(4)	
Cl(2)–Ru–P(1)	120.92(4)	
Cl(2)–Ru–P(2)	79.53(4)	
P(1)–Ru–P(2)	76.63(4)	82.30(5)
N(1)–Ru–P(1)		94.43(14)
N(1)–Ru–P(2)		88.0(2)
Ru–N(1)–O(1)		174.1(4)

[a] Angular brackets indicate mean values.

The $^{13}C\{^1H\}$ NMR spectra of **3**–**6** contain no surprising features and it is sufficient to point out the marked low-field chemical shifts of the ring carbon resonances of $C_5Me_5^-$ appearing at 112.4, 113.5, 115.5 and 101.2 ppm, respectively, indicative of a high oxidation state of Ru. The corresponding carbon resonances in the Ru(II) complexes **1** and $Ru(\eta^5\text{-}C_5Me_5)_2$ appear at 89.6 and 82.9 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectra of **3**–**5** exhibit a singlet at 75.62, 60.66 and 66.35 ppm, respectively, with respect to PPh_3 (for comparison, the corresponding phosphorus resonance of complex **1** is found at 27.22 ppm). The IR spectrum of **5** contains a strong band at 1850 cm^{-1} characteristic of a linear Ru–N–O arrangement. In the similar complexes $[Ru(NO)(\eta^5\text{-}C_5H_5)(PMe_3)_2](PF_6)_2$, $[Ru(NO)(\eta^5\text{-}C_5H_5)(PPh_3)_2]\text{-}(PF_6)_2$ and $[Ru(NO)(\eta^5\text{-}C_5Me_5)(PPh_3)_2](BF_4)_2$, the ν(NO) stretching frequencies are found at 1875, 1850 and 1805 cm^{-1}, respectively [8,12].

Some further comments on the assignment of the oxidation state of Ru in the complexes under consideration are in order here. For complexes **3**, **4** and **6**, obtained via oxidative addition of O_2, Cl_2 and H_2, respectively, the electron deficiency of the metal center (formally a +IV oxidation state) is supported by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic evidence. The situation of **5**, however, is less clear. **5** is obtained either by reaction of **2** with NO or by reaction of **1** with NO^+. The latter reaction is, at least formally, a simple substitution process rather than an oxidative addition. It has become conventional to interpret a linear M–N–O arrangement in terms of coordination of NO^+, implying that complex **5** contains formally Ru(II). The diamagnetic behavior is indeed not conclusive as it is consistent with either Ru(II) or Ru(IV). The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **5**, by contrast, strongly resemble any of the other complexes (**3**, **4** and **6**), exhibiting significantly downfield-shifted ring carbon resonances of $C_5Me_5^-$ and phosphorus resonances of dppe. Add to this the fact that the bond order of NO in **5** is closer to NO than to NO^+ (cf., free NO and NO^+ exhibit the ν(NO) stretching frequency at 1876 and 2220 cm^{-1}, respectively). This reaction can therefore be better envisioned as an oxidative addition resulting in at least a Ru(II) oxidation state. Therefore, the NO moiety may be better described as NO or even NO^- rather than as NO^+, despite the linear Ru–N–O arrangement.

3.2. X-ray crystallography

The crystal structure of **3** (O_2 coordinated in η^2-fashion) has been published recently [1] and is not discussed here. It is worth mentioning, however, that very recently the synthesis of related η^2-dioxygen complexes of the type $[Ru(H)(\eta^2\text{-}O_2)(L\text{–}L)_2]^+$ (L–L = 1,2-bis(diisopropylphosphino)ethane, 1,2-bis(dicyclohexylphosphino)ethane) has been reported [13].

The structure of the dichloride Ru(IV) complex **4b** is shown in Fig. 1. Selected bond lengths and angles are given in Table 4. It features a Ru cation in a half-sandwich 'four-

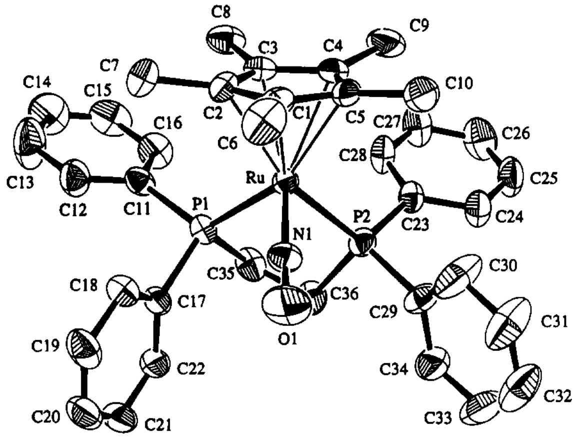

Fig. 2. ORTEP plot (30% ellipsoids) of $[Ru(NO)(\eta^5\text{-}C_5Me_5)(dppe)](CF_3SO_3)_2 \cdot CH_3NO_2$ (**5b**) ($CF_3SO_3^-$ and CH_3NO_2 omitted for clarity).

legged' piano-stool configuration. The Ru–P(1) and Ru–P(2) distances are significantly different, being 2.351(1) and 2.403(1) Å, respectively, with a P(1)–Ru–P(2) angle of 76.63(4)° (cf., in complex **3**, Ru–P(1) = 2.349(1) Å, Ru–P(2) = 2.348(1) Å and P(1)–Ru–P(2) = 79.9(1)°). This appears to be merely a solid state effect since the $^{31}P\{^1H\}$ NMR solution spectrum of **4** exhibits only one singlet. The Ru–Cl distances are only slightly different, Ru–Cl(1) = 2.397(1) and Ru–Cl(2) = 2.390(1) Å, respectively, and the Cl(1)–Ru–Cl(2) angle is 79.86(4)°. The Ru–Cl bond lengths are comparable to other Ru(IV) dichloride complexes. For instance, the Ru–Cl(1) and Ru–Cl(2) distances in $[Ru(Cl)_2(\eta^5\text{-}C_5Me_5)(SC_4H_8)_2]ClO_4$ are 2.369(1) and 2.391(1) Å [14], and in $Ru(Cl)_2(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_4H_4OMe)$ the Ru–Cl distance is 2.403(1) Å [15].

The molecular structure of **5b**, as depicted in Fig. 2, confirms the piano-stool configuration with the NO ligand bonded via nitrogen. Selected bond lengths and angles are given in Table 4. The distances Ru–P(1) and Ru–P(2) are 2.415(1) and 2.393(1) Å, respectively, with a P(1)–Ru–P(2) angle of 82.30(5)°. The N(1)–Ru–P(1) and N(1)–Ru–P(2) angles are 94.4(1) and 88.0(2)°, respectively. The linear Ru–N–O arrangement (174.1(4)°) has Ru–N and N–O distances of 1.748(4) and 1.141(5) Å, respectively, which is consistent with the high ν(NO) frequency of 1850 cm^{-1}. These values are in the range observed also for other nitrosyl complexes [16,17].

4. Supplementary material

Listings of anisotropic temperature factors, hydrogen atom parameters, complete bond distances and angles can be obtained from the authors on request.

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