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Organometallic chelating ligands. Synthesis of a new anionic tripod like ligand with an N,N′,O-donor set. X-ray crystal structure of $[(\eta^6\text{-}C_6Me_6)Ru\{\mu\text{-}P(O)(OMe)_2\}(\mu\text{-}Pz)_2Re(CO)_3]$ (Me = methyl, Pz = pyrazolate)*

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Abstract

The synthesis of the new anionic organometallic chelating ligand $[(\eta^6\text{-}C_6Me_6)Ru\{P(O)(OMe)_2\}(Pz)_2]^- = L^-$ (Me = methyl, Pz = pyrazolate) is described. This ligand was isolated as its neutral sodium derivative NaL· ~0.7$NaPF_6$, which is a new synthetic precursor for obtaining heterobimetallic complexes with phosphonate and pyrazolate groups acting as bridging ligands. The heterobimetallic compound $LRe(CO)_3$ was obtained by reaction of $ReBr(CO)_5$ with NaL· ~0.7$NaPF_6$, in which the anionic complex L^- is acting as an N,N′,O-tripod donor ligand. The structure of the title complex was established by X-ray crystallography. The compound crystallizes as monoclinic, space group *Cc* (No. 9) with $a = 31.214(6)$, $b = 11.111(2)$, $c = 15.769(3)$ Å, $\beta = 103.14(3)°$. The neutral complex has a binuclear structure with the $(C_6Me_6)Ru$ and $Re(CO)_3$ moieties triply bridged by two pyrazolate groups and one phosphonate group. The synthesis of TlPz is also described.

Key words: Crystal structures; Ruthenium complexes; Polydentate ligand complexes; Tripod ligand complexes; Arene complexes; Carbonyl complexes

Introduction

Many binuclear complexes containing pyrazolate or pyrazolate derivatives as bridging ligands have been reported in recent years. The properties of these anions as binucleating agents have been well demonstrated [1]. Several of these complexes are very stable and some of them show catalytic activity in the homogeneous phase, for example in hydroformylation reactions of olefins [2].

The general routes of synthesis of these complexes containing exobidentate pyrazolate groups as bridging ligands, can be resumed as follows:

$$[M]\text{–}X\text{–}[M] \xrightarrow[-HX]{HPz} [M]\text{–}Pz\text{–}[M] \quad \text{refs. 1a, 3–5}$$

$$[M]\text{–}PzH + B\text{–}[M'] \xrightarrow[-HB]{} [M]\text{–}Pz\text{–}[M'] \quad \text{ref. 6.}$$

$X = Cl^-$, OMe^-, OH^-; Pz = pyrazolate ($C_3H_3N_2$); B = $acac^-$, OMe^-; [M], [M′] = organometallic fragment

Recently we reported the synthesis and reactivity of a new organometallic anionic N,O,O′-donor ligand of formula $[(\eta^5\text{-}C_5Me_5)Rh\{P(O)(OMe)\}_2(Pz)]^-$. This ligand, isolated as its thallium or sodium derivative, allows access to the synthesis of heterobimetallic complexes with phosphonate and pyrazolate groups as bridging ligands. It was demonstrated too that this anion acts as a tridentate N,O,O′-tripod-like ligand [7].

This paper describes the synthesis of the new organometallic anionic tripod ligand $[(\eta^6\text{-}C_6Me_6)Ru\{P(O)(OMe)_2\}(Pz)_2]^- = L^-$, which was isolated as its sodium derivative NaL· ~0.7$NaPF_6$. During this work we prepared TlPz, which is an excellent compound to

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*Dedicated to Professor Helmut Werner on the occasion of his 60th birthday.

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coordinate the anion pyrazolate to an organometallic fragment that contains terminal halogen ligands.

We also report the characterization of [(η^6-C_6Me_6)-Ru{μ-P(O)(OMe)$_2$}(μ-Pz)$_2$Re(CO)$_3$] by single-crystal X-ray diffraction. This structure demonstrates the potentiality of the new organometallic anion to act as a tridentate N,N′,O-donor ligand which provides a good synthetic tool to obtain heterobimetallic complexes of ruthenium and other metal centers, with two pyrazolate as exobidentate bridging ligands.

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. [(η_6-C_6Me_6)RuCl$_2${P(OH)(OMe)$_2$}] was prepared as previously described [8].

IR spectra were recorded on a Bruker IFS-25 spectrophotometer. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AC200 spectrometer and chemical shifts are reported relative to $SiMe_4$ and 85% H_3PO_4 (positive shifts downfield), respectively. Elemental analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Solvents were dried and distilled before use.

Preparation of TlPz, Pz = $C_3H_3N_2$

Sodium (168 mg, 7.34 mmol) was added to a solution of pyrazol (500 mg, 7.34 mmol) in 20 ml of methanol. The mixture was stirred at room temperature and $TlNO_3$ (1.956 g, 7.34 mmol) was added after all the sodium had reacted. After stirring the suspension for 2 h at room temperature the solvent was evaporated to dryness and the residue extracted with benzene in a Sohxlet apparatus. The benzene suspension was evaporated to dryness and the residue dried *in vacuo*. Yield 1.5 g (76%) of a white moisture sensitive powder. *Anal.* Found: C, 12.95; H, 1.08; N, 10.20. Calc. for $C_3H_3N_2Tl$: C, 13.2; H, 1.11; N, 10.32%. ^{1}H NMR δ 7.12 (d, 2H, $H_{3/5}$, ^2J(HH) = 1.98 Hz) and 6.00 (t, 1H, H_4).

Preparation of [(η^6-C_6Me_6)RuCl{P(O)(OMe)$_2$}(PzH)] (1)

$TlC_3H_3N_2$ (842 mg, 3.10 mmol) was added to a solution of complex [(η^6-C_6Me_6)RuCl$_2${P(OH)(OMe)$_2$}] (1.3 g, 2.925 mmol) in 50 ml of dichloromethane. After stirring for 19 h at room temperature, the TlCl formed was filtered through Kieselguhr and the clear orange filtrate concentrated to about 5 ml. Addition of n-hexane gave an orange precipitate, which was filtered, washed with n-hexane and dried *in vacuo*. Recrystallization at −25 °C from CH_2Cl_2/n-hexane gave orange air-stable crystals. Yield 1.22 g (88%). *Anal.* Found: C, 42.61; H, 5.97; N, 5.55. Calc. for $C_{17}H_{28}ClN_2O_3PRu$: C, 42.86; H, 5.93; N, 5.88%. IR (KBr): ν(P=O), 1115; ν(N–H), 3191 cm^{-1}.

Preparation of [(η^6-C_6Me_6)Ru{P(O)(OMe)$_2$}(Pz)(PzH)] (2)

$TlC_3H_3N_2$ (736 mg, 2.714 mmol) was added to a solution of complex **1** (1.292 g, 2.714 mmol) in 50 ml of dichloromethane. The mixture was boiled under reflux for 5 h. The thallium chloride formed was filtered off through Kieselguhr and the solution was concentrated to about 5 ml. Addition of n-hexane gave a yellow precipitate, which was filtered off, washed with n-hexane and dried *in vacuo*. Recrystallization at −25 °C from CH_2Cl_2/n-hexane gave yellow air-stable crystals. Yield 1.294 g (94%). *Anal.* Found: C, 46.95; H, 6.26; N, 10.75%. Calc. for $C_{20}H_{31}N_4O_3PRu$: C, 47.29; H, 6.26; N, 10.98%. IR (KBr): ν(P=O), 1115; ν(N–H), 3199 cm^{-1}.

Preparation of [(η^6-C_6Me_6)Ru{P(O)(OMe)$_2$}(PzH)$_2$]-PF_6 (3)

A solution of complex [(η^6-C_6Me_6)RuCl$_2${P(OH)-(OMe)$_2$}] (500 mg, 1.125 mmol) in 50 ml of acetone was treated with silver hexafluorophosphate (569 mg, 2.25 mmol) and with an excess of pyrazole (182 mg, 2.67 mmol). The resulting mixture was boiled under reflux for 17 h in the absence of light. The silver chloride formed was filtered off through Kieselguhr and the solution obtained concentrated under reduced pressure to a small volume. The complex was precipitated by addition of diethyl ether. The microcrystalline yellow solid was washed with diethyl ether and dried *in vacuo*. Yield 462 mg (63%). *Anal.* Found: C, 36.97; H, 5.17%. Calc. for $C_{20}H_{32}F_6N_4O_3P_2Ru$: C, 36.76; H, 4.94%. IR (KBr): ν(P=O), 1035; ν(N–H), 3300; ν(PF_6^-), 835 and 574 cm^{-1}.

Preparation of [(η^6-C_6Me_6)Ru{P(O)(OMe)$_2$}(Pz)$_2$Na]·~0.7NaPF$_6$ (4)

An excess of sodium hydride (15 mg of 80% dispersion in mineral oil; 0.63 mmol) was added to a cooled suspension (−20 °C) of complex **3** (150 mg, 0.23 mmol) in 25 ml of 1,2-dimethoxyethane (freshly distilled). The mixture was stirred until the evolution of hydrogen had ceased. The excess of sodium hydride was filtered off through Kieselguhr at room temperature and the solution evaporated to dryness. The solid residue was extracted with dichloromethane and the clear solution concentrated under reduced pressure to a small volume. The complex was precipitated by addition of diethyl ether or n-hexane. The microcrystalline yellow solid was washed with diethyl ether and dried *in vacuo*. Yield 90 mg. *Anal.* Found: C, 36.57; H, 4.50. Calc. for $C_{20}H_{30}N_4NaO_3PRu\cdot0.7NaPF_6$: C, 34.44; H, 4.33%. IR (KBr): ν(P=O), 1136 cm^{-1}.

Preparation of $[(\eta^6\text{-}C_6Me_6)Ru\{\mu\text{-}P(O)(OMe)_2\}(\mu\text{-}Pz)_2Re(CO)_3]$ (5)

A suspension of complex **3** (90 mg, 0.14 mmol) in 15 ml of 1,2-dimethoxyethane (freshly distilled) was treated with a large excess of sodium hydride (9 mg of 80% dispersion in mineral oil; 0.40 mmol) at low temperature (−20 °C). The mixture was stirred until the evolution of hydrogen had ceased. The excess of sodium hydride was filtered off through Kieselguhr and the solution evaporated to dryness. The residue was dissolved in dichloromethane and the stoichiometric amount of $ReBr(CO)_5$ (56 mg, 0.14 mmol) was added. The mixture was boiled under reflux for 17 h and the solution was chromatographed on Kieselgel (HF_{254}, type 60) using dichloromethane as eluent. The solution obtained was concentrated to a small volume and precipitated with n-hexane. Orange crystals were obtained from dichloromethane–hexane. Yield 60 mg (55%). *Anal.* Found: C, 35.73; H, 4.02. Calc. for $C_{23}H_{30}N_4O_6PReRu$: C, 35.56; H, 3.89%. IR (KBr): ν(P=O), 1188; ν(CO), 2000, 1882, 1867 and 1860 cm^{-1}. IR (CH_2Cl_2): ν(CO), 2011, 1889 and 1877 cm^{-1}.

Crystal structure determination of 5

A deep-orange, parallelepiped-shaped, single crystal of average dimensions 0.38 × 0.28 × 0.20 mm was selected for structure determination by X-ray diffraction. Intensity data were collected on a Siemens R3m/V four-circle diffractometer, ω scan mode, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Two standard reflections, monitored every 98 reflections, showed no significant intensity variation during data collection. Cell parameters were determined from a least-squares fit of 22 reflections with $3.9 \leqslant 2\theta \leqslant 24.1°$. A total of 5212 reflections was collected for structure analysis with $3.0 \leqslant 2\theta \leqslant 50.0°$ ($0 \leqslant h \leqslant 37$, $0 \leqslant k \leqslant 13$, $-18 \leqslant l \leqslant 18$) and merged to give 4758 independent reflections ($R_{int} = 0.018$) of which 4171 reflections with $I > 2\sigma(I)$ were considered observed. Corrections were applied for Lorentz and polarization effects; empirical correction for absorption was applied with maximum and minimum transmission factors 0.165 and 0.108, respectively.

A summary of the crystal data is presented in Table 1. The structure was solved using direct methods and refined on F. Non-H atoms were refined first isotropically by least-squares full-matrix and then anisotropically by least-squares block-matrix. H atoms were placed on calculated positions and allowed to ride on their parent C atoms with C–H = 0.96 Å and fixed isotropic $U = 0.08$ $Å^2$. The total number of parameters refined was 647. Refinement converged to final $R = 0.048$ and $R_w = 0.068$, (weighting scheme $w^{-1} = \sigma^2(F) + 0.0041F^2$), and $S = 0.94$. Largest and mean Δ/σ were 0.073 and 0.006, respectively. The highest residuals in the final difference synthesis were found in the vicinity of the heavy atoms, extreme values being 2.17 and −2.14 e $Å^3$. All calculations were performed with the Siemens SHELXTL PLUS (PC version) [9].

TABLE 1. Crystal data for $[(\eta^6\text{-}C_6Me_6)Ru\{\mu\text{-}P(O)(OMe)_2\}(\mu\text{-}Pz)_2Re(CO)_3]$

Empirical formula	$C_6(CH_3)_6Ru(C_3H_3N_2)_2PO\text{-}(OCH_3)_2Re(CO)_3$
Crystal system	monoclinic
Space group	*Cc*
Unit cell dimensions	
a (Å)	31.214(6)
b (Å)	11.111(2)
c (Å)	15.769(3)
β (°)	103.14(3)
Volume ($Å^3$)	5326(2)
Z	8
Formula weight	776.8
Density (calc.) (Mg/m^3)	1.937
Absorption coefficient (mm^{-1})	5.213
F(000)	3024

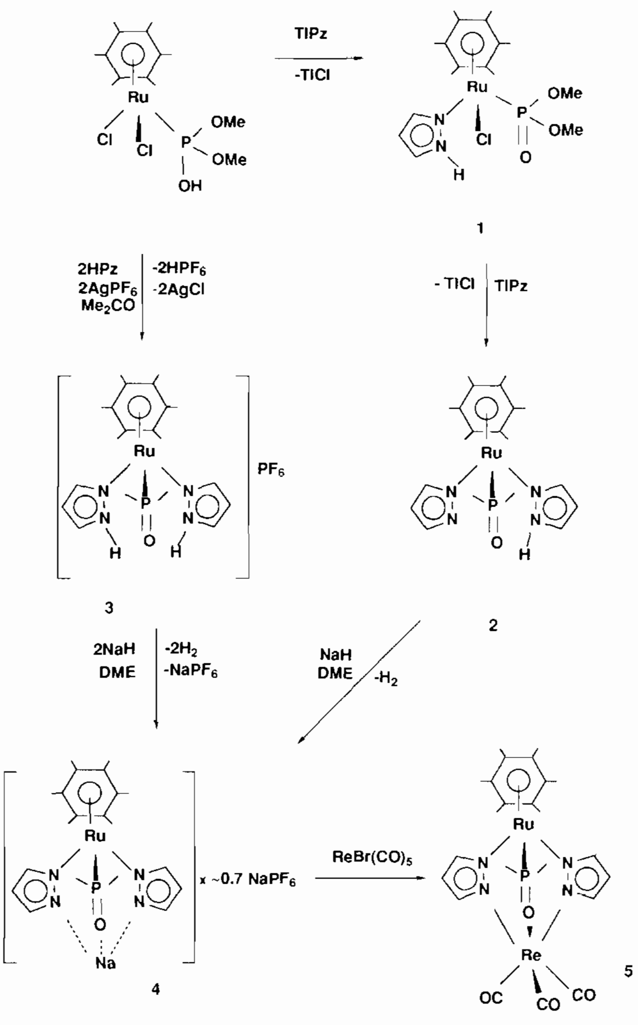
Results and discussion

The neutral complex $[(\eta^6\text{-}C_6Me_6)RuCl_2\{P(OH)(OMe)_2\}]$ reacts in dichloromethane solution with thallium pyrazolate (TlPz) in molar ratio 1:1 to give the complex $[(\eta^6\text{-}C_6Me_6)RuCl\{P(O)(OMe)_2\}(PzH)]$ (**1**). This compound reacts with a stoichiometric amount of TlPz in refluxing dichloromethane with formation of the neutral complex $[(\eta^6\text{-}C_6Me_6)Ru\{P(O)(OMe)_2\}(Pz)(PzH)]$ (**2**). The direct reaction of the starting complex with TlPz in molar ratio 1:2 gives a mixture of complexes **1** and **2** together with other uncharacterized compounds.

Thallium pyrazolate was prepared by the reaction of pyrazole and sodium methoxide following by a metathetical reaction with thallium nitrate in methanol solution, according to:

$$HPz + NaOMe \xrightarrow[-MeOH]{} NaPz \xrightarrow[-NaNO_3]{TlNO_3} TlPz$$

On the other hand, treatment of the neutral complex $[(\eta^6\text{-}C_6Me_6)RuCl_2\{P(OH)(OMe)_2\}]$ in acetone solution with silver hexafluorophosphate in the presence of an excess of pyrazole, involves the precipitation of silver chloride, the loss of HPF_6 and the formation of the monocationic complex $[(\eta^6\text{-}C_6Me_6)Ru\{P(O)(OMe)_2\}(PzH)_2]PF_6$ (**3**). As expected, when complexes **2** and **3** react with a slight excess of sodium hydride in 1,2-dimethoxyethane (DME) at low temperature (−25 °C) an immediate evolution of hydrogen was observed. If the solid obtained by evaporation to dryness of the DME solution is dissolved in dichloromethane and n-hexane is added to this solution, the formation of



Scheme 1.

$[(\eta_6\text{-}C_6Me_6)Ru\{P(O)(OMe)_2\}(Pz)_2Na]\cdot{\sim}0.7NaPF_6$ (**4**) is observed ($^{31}P\{^1H\}$ NMR: intensity relation signals $P(O)(OMe)_2/PF_6 = 1{:}0.7$). The property of incorporating sodium salts was previously observed for similar organometallic anionic complexes [8, 10, 11]. It was possible to remove the inorganic salt by its reprecipitation from organic solvents. Thus, a previous extraction with methanol of the DME solid residue and further addition of n-hexane, led to the formation of the expected sodium derivative $[(\eta^6\text{-}C_6Me_6)Ru\{P(O)(OMe)_2\}(Pz)_2Na]$. This sodium compound is more unstable to moisture than complex **4** and it was only characterized by NMR spectroscopy (^1H NMR ($CDCl_3$): δ 1.89 (d, C_6Me_6, $^4J(PH) = 1.0$ Hz), 2.99 (d, OCH_3, $^3J(PH) = 10.9$ Hz), 3.04 (d, OCH_3, $^3J(PH) = 10.9$ Hz), 6.22 (t, H_4), 7.55 (d, H_5, $J(HH) = 1.7$ Hz) and 7.66 (d, H_3, $J(HH) = 2.2$ Hz] ppm.

All attempts to carry out a metathetical reaction of **4** with thallium nitrate in methanol or 1,2-dimethoxyethane to obtain the neutral heterobimetallic derivative $[(\eta^6\text{-}C_6Me_6)Ru\{P(O)(OMe)_2\}(Pz)_2Tl]$ failed. However, the utility of the sodium complex **4** for further synthetic purposes was demonstrated by its reaction with $ReBr(CO)_5$ to give the corresponding heterobimetallic complex $[(\eta^6\text{-}C_6Me_6)Ru\{\mu\text{-}P(O)(OMe)_2\}(\mu\text{-}Pz)_2Re(CO)_3]$ (**5**). All these reactions are represented in Scheme 1.

The new complexes were characterized by elemental analyses and IR and NMR spectra. In particular the IR spectra show the presence of the $\nu(P{=}O)$ and $\nu(N\text{–}H)$ (**1**–**3**) bands. The IR spectrum of complex **5** in the solid state shows four carbonyl stretching frequencies and in dichloromethane solution only shows three bands (see 'Experimental'). For complexes of the

TABLE 2. NMR chemical shifts (δ, ppm) and coupling constants (Hz) of isolated complexes[a]

Complex	Solvent	^1H NMR					$^{31}P\{^1H\}$ NMR
		$C_6Me_6(^4J(PH))$	$CH_3OP(^3J(PH))$	Pyrazolate			
				$H_3(J(HH))$	$H_5(J(HH))$	H_4	
1	CD_2Cl_2	1.98 d[1.0]	3.12 d[10.9] 3.70 d[10.9]	7.72 d[2.0]	7.55 d[2.0]	6.36 t	98.54 s
2	$CDCl_3$	1.62 d[1.2]	3.10 d[10.9]	7.84 d[2.0]	7.64 d[2.3]	6.25 t	96.62 s
3[b]	$CDCl_3$	2.04 d[1.0]	3.57 d[10.9] 3.63 d[10.9]	7.70 d[2.6]	7.59 d[2.1]	6.40 t	98.80 s
4[c]	$CDCl_3$	1.86 s,br	3.60 d[10.2] 3.54 d[10.2]	7.71 s,br	7.551 s,br	6.31 t	95.10 s
5	$CDCl_3$	2.14 s,br	3.33 d[11.0]	7.86 d[2.1]	7.54 d[2.0]	6.13 t	107.55 s

[a] Chemical shifts relative to Me_4Si and H_3PO_4 85% as external standard; s = singlet, d = doublet, t = triplet, br = broad. [b] ^1H NMR: δ 13.02 ppm (s, br, HN); $^{31}P\{^1H\}$ NMR: δ −145.08 ppm (sept., PF_6^-, $J(PF) = 712.6$ Hz). [c] $^{31}P\{^1H\}$ NMR: δ −144.86 ppm (sept., PF_6^-, $J(PF) = 716.67$ Hz).

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$), with e.s.d.s in parentheses

	x	y	z	$U_{eq}{}^a$
Molecule A				
Re	3901	2853(1)	5022	37(1)
Ru	4171(1)	6434(1)	4789(1)	31(1)
P	4174(2)	5445(5)	6047(3)	34(2)
O(1)	4047(5)	4161(14)	6038(9)	44(5)
O(2)	3870(6)	6129(14)	6555(10)	51(6)
O(3)	4639(5)	5543(15)	6778(10)	51(5)
O(4)	4565(8)	1024(26)	6041(19)	114(12)
O(5)	3809(7)	1133(18)	3522(13)	69(7)
O(6)	3184(7)	1550(14)	5605(15)	73(8)
N(1)	3599(6)	5459(14)	4177(11)	39(6)
N(2)	3510(5)	4256(13)	4326(11)	35(5)
N(3)	4529(6)	4960(16)	4451(10)	38(6)
N(4)	4460(6)	3765(15)	4592(12)	42(6)
C(1)	4739(9)	7770(23)	4861(21)	65(10)
C(2)	4493(9)	7872(19)	3978(18)	54(9)
C(3)	4044(10)	8065(22)	3790(17)	55(10)
C(4)	3830(8)	8325(17)	4491(13)	41(7)
C(5)	4075(7)	8305(22)	5324(16)	50(8)
C(6)	4531(9)	8034(23)	5579(16)	53(9)
C(7)	5228(8)	7583(31)	5119(22)	80(12)
C(8)	4743(11)	7794(27)	3247(20)	76(12)
C(9)	3823(11)	8249(28)	2887(15)	71(11)
C(10)	3356(9)	8657(20)	4310(19)	60(10)
C(11)	3850(11)	8738(24)	6084(19)	71(11)
C(12)	4809(12)	8107(29)	6501(20)	85(13)
C(13)	3843(10)	5742(28)	7389(17)	71(11)
C(14)	5006(8)	4946(39)	6676(21)	95(15)
C(15)	3246(8)	5895(23)	3665(16)	55(9)
C(16)	2921(7)	5073(20)	3447(12)	42(7)
C(17)	3106(7)	4040(23)	3870(13)	48(8)
C(18)	4880(7)	4989(20)	4103(16)	45(8)
C(19)	5030(8)	3960(25)	3951(15)	55(9)
C(20)	4752(8)	3108(26)	4259(18)	56(9)
C(21)	4325(10)	1705(22)	5636(18)	61(10)
C(22)	3841(9)	1764(20)	4039(14)	47(8)
C(23)	3467(8)	2071(23)	5406(17)	55(9)
Molecule B				
Re	1642(1)	3364(1)	6668(1)	38(1)
Ru	1790(1)	7014(1)	6599(1)	27(1)
P	1199(2)	5950(5)	5925(3)	34(2)
O(1)	1219(5)	4574(13)	5890(10)	45(5)
O(2)	1035(5)	6365(14)	4949(10)	49(5)
O(3)	777(5)	6277(15)	6281(11)	51(6)
O(4)	972(8)	1940(19)	7333(16)	87(9)
O(5)	2370(8)	1786(19)	7811(17)	95(9)
O(6)	1639(12)	1601(20)	5190(16)	115(13)
N(1)	2225(5)	5667(15)	6288(10)	36(5)
N(2)	2165(5)	4454(15)	6289(12)	43(6)
N(3)	1774(5)	5923(14)	7676(10)	30(5)
N(4)	1721(6)	4655(14)	7669(11)	38(6)
C(1)	1587(8)	8717(18)	7163(15)	43(7)
C(2)	2066(7)	8781(18)	7449(14)	40(7)
C(3)	2318(8)	8620(17)	6835(16)	49(8)
C(4)	2101(8)	8516(17)	5926(14)	43(7)
C(5)	1646(10)	8620(22)	5666(15)	56(9)
C(6)	1407(8)	8716(16)	6262(12)	36(6)
C(7)	1288(8)	8867(26)	7825(15)	59(9)
C(8)	2300(10)	9022(25)	8405(16)	74(11)
C(9)	2812(9)	8734(23)	7189(19)	64(10)
C(10)	2393(12)	8519(37)	5221(19)	94(15)
C(11)	1453(8)	8740(20)	4724(13)	47(8)
C(12)	908(9)	8993(30)	5953(22)	81(12)
C(13)	682(8)	5756(25)	4388(18)	63(9)
C(14)	694(10)	5792(30)	7007(19)	72(11)
C(15)	2613(7)	5882(23)	6103(13)	44(7)
C(16)	2791(8)	4835(26)	5936(17)	57(10)
C(17)	2538(8)	3929(24)	6044(17)	56(9)
C(18)	1805(8)	6320(19)	8501(12)	40(7)
C(19)	1775(8)	5378(22)	9056(11)	46(8)
C(20)	1717(9)	4357(18)	8532(13)	55(9)
C(21)	1215(10)	2516(23)	7076(16)	65(10)
C(22)	2107(9)	2355(17)	7361(15)	50(8)
C(23)	1650(12)	2253(18)	5728(16)	68(11)

(*continued*)

TABLE 3. (*continued*)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

type [LRe(CO)$_3$], where L$^-$ is a symmetrical tripod ligand, two carbonyl bands are usually observed (A and E modes of an ideal C_{3v} local symmetry) [12]. In our case the lack of symmetry of the tripod ligand L$^-$ probably causes the splitting of the E band.

The ^{1}H NMR spectra (Table 2) are consistent with the proposed formulation of compounds **1–5**, showing the inequivalence of the protons of the pyrazole groups, the presence of a doublet signal for the C_6Me_6 ligand and two doublets due to the presence of non-isochronous OMe groups. The ^{31}P NMR decoupled spectra show the expected singlet signal assigned to the phosphonate group (Table 2).

Crystal structure of complex [(η^6-C_6Me_6)Ru{μ-P(O)(OMe)$_2$}(μ-Pz)$_2$Re(CO)$_3$]

Atomic coordinates and equivalent isotropic thermal parameters of non-H atoms are listed in Table 3, with relevant bond distances and angles in Table 4. There are two independent molecules (A and B) per asymmetric unit which do not differ significantly in their geometry. Molecules A and B, in their actual relative orientations, showing the atom labelling scheme, are represented in Fig. 1.

The neutral complex has a binuclear structure with intermetallic separation Re–Ru equal to 4.102(3) and 4.086(2) Å for molecules A and B, respectively. These distances exclude any significant metal–metal interaction. The Re–Ru vectors of the independent molecules are nearly parallel to each other with a small deviation of 7.2°, and roughly oriented in the direction of the short b axis of the crystal. The ruthenium and rhenium atoms are triply bridged by two pyrazolate groups (Pz(1) and Pz(2)) and one phosphonate group. The coordi-

TABLE 4. Selected bonds distances (Å) and bonds angles (°), with e.s.d.s in parentheses

	A	B		A	B
Re–O(1)	2.13(2)	2.08(1)	Ru–P(1)	2.27(1)	2.25(1)
Re–N(2)	2.13(2)	2.22(2)	Ru–N(1)	2.13(2)	2.15(2)
Re–N(4)	2.25(2)	2.11(2)	Ru–N(3)	2.12(2)	2.10(2)
Re–C(21)	1.93(3)	1.86(3)	Ru–C(1)	2.29(3)	2.24(2)
Re–C(22)	1.94(2)	1.96(2)	Ru–C(2)	2.40(3)	2.42(2)
Re–C(23)	1.83(3)	1.93(2)	Ru–C(3)	2.37(3)	2.40(2)
P–O(1)	1.48(2)	1.53(2)	Ru–C(4)	2.35(2)	2.31(2)
P–O(2)	1.57(2)	1.58(2)	Ru–C(5)	2.29(2)	2.29(2)
P–O(3)	1.64(2)	1.59(2)	Ru–C(6)	2.31(2)	2.24(2)
O(2)–C(13)	1.40(3)	1.42(3)	O(3)–C(14)	1.36(4)	1.34(4)
O(4)–C(21)	1.15(4)	1.14(4)	C(1)–C(2)	1.44(4)	1.46(3)
O(5)–C(22)	1.06(3)	1.15(3)	C(1)–C(7)	1.50(4)	1.56(4)
O(6)–C(23)	1.15(4)	1.11(3)	C(2)–C(3)	1.38(4)	1.39(4)
N(1)–N(2)	1.40(2)	1.36(2)	C(2)–C(8)	1.53(5)	1.54(3)
N(1)–C(15)	1.30(3)	1.33(3)	C(3)–C(4)	1.44(4)	1.44(3)
N(2)–C(17)	1.32(3)	1.43(3)	C(3)–C(9)	1.45(3)	1.52(4)
C(15)–C(16)	1.35(3)	1.34(4)	C(4)–C(5)	1.36(3)	1.39(4)
C(16)–C(17)	1.39(3)	1.32(4)	C(4)–C(10)	1.49(4)	1.59(5)
N(3)–N(4)	1.37(2)	1.42(2)	C(5)–C(6)	1.42(3)	1.33(4)
N(3)–C(18)	1.33(3)	1.36(2)	C(5)–C(11)	1.60(4)	1.48(3)
N(4)–C(20)	1.36(3)	1.40(3)	C(6)–C(1)	1.46(4)	1.40(3)
C(18)–C(19)	1.28(4)	1.38(3)	C(6)–C(12)	1.52(4)	1.55(4)
C(19)–C(20)	1.44(4)	1.39(3)			
O(1)–Re–N(2)	83.5(6)	84.0(6)	C(21)–Re–C(22)	85.4(10)	90.9(11)
O(1)–Re–N(4)	82.7(6)	87.3(6)	C(21)–Re–C(23)	89.8(12)	94.5(13)
N(2)–Re–N(4)	84.7(6)	82.0(7)	C(22)–Re–C(23)	91.4(12)	85.7(10)
Re–O(1)–P	132.4(9)	130.6(8)	Re–C(21)–O(4)	175.9(29)	175.8(25)
Re–N(2)–N(1)	132.6(12)	130.6(14)	Re–C(22)–O(5)	177.2(23)	175.7(24)
Re–N(4)–N(3)	130.2(14)	132.5(13)	Re–C(23)–O(6)	176.4(22)	177.4(27)
P–Ru–N(1)	89.2(5)	91.1(4)	Ru–P–O(1)	120.7(6)	120.5(6)
P–Ru–N(3)	87.0(5)	84.9(4)	Ru–P–O(2)	109.2(6)	111.0(6)
N(1)–Ru–N(3)	85.9(7)	85.1(6)	Ru–P–O(3)	114.2(7)	111.8(6)
P–O(2)–C(13)	120.1(17)	120.3(16)	O(2)–P–O(3)	98.6(9)	99.6(9)
P–O(3)–C(14)	121.2(17)	123.1(17)			
N(2)–N(1)–C(15)	106.8(17)	108.1(18)	N(4)–N(3)–C(18)	105.3(18)	108.2(15)
N(1)–N(2)–C(17)	106.4(16)	106.4(18)	N(3)–N(4)–C(20)	108.2(20)	104.8(15)
N(1)–C(15)–C(16)	112.8(22)	109.0(22)	N(3)–C(18)–C(19)	115.2(22)	111.2(18)
C(15)–C(16)–C(17)	103.3(18)	110.5(26)	C(18)–C(19)–C(20)	104.5(23)	105.1(17)
C(16)–C(17)–N(2)	110.7(20)	105.9(23)	C(19)–C(20)–N(4)	106.5(23)	110.7(18)
C(6)–C(1)–C(2)	120.1(24)	117.2(22)	C(3)–C(4)–C(5)	118.5(23)	120.3(23)
C(6)–C(1)–C(7)	115.1(25)	121.1(20)	C(3)–C(4)–C(10)	121.2(20)	118.5(22)
C(2)–C(1)–C(7)	124.1(30)	120.9(19)	C(5)–C(4)–C(10)	120.3(23)	120.3(21)
C(1)–C(2)–C(3)	120.9(28)	118.7(19)	C(4)–C(5)–C(6)	125.7(25)	119.8(21)
C(1)–C(2)–C(8)	118.2(24)	122.3(22)	C(4)–C(5)–C(11)	118.3(22)	117.4(25)
C(3)–C(2)–C(8)	120.9(24)	119.0(21)	C(6)–C(5)–C(11)	115.8(21)	122.5(24)
C(2)–C(3)–C(4)	119.4(23)	119.2(21)	C(5)–C(6)–C(1)	114.7(21)	123.8(22)
C(2)–C(3)–C(9)	117.7(29)	114.9(21)	C(5)–C(6)–C(12)	125.4(26)	118.5(20)
C(4)–C(3)–C(9)	121.5(26)	125.5(21)	C(1)–C(6)–C(12)	119.7(25)	117.3(22)

nation spheres of the metals are completed by a hexamethylbenzene ring on the Ru atom, and three terminal carbonyl groups on the Re atom.

The Ru atoms exhibit a pseudo-octahedral geometry, commonly referred as 'piano-stool' configuration [3c, 4, 13]. The Ru–C(ring) contacts (Table 3) compare well with those found in the related complex $[\{(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)[\mu\text{-}P(O)(OMe)_2]_2\}_2Cu]\cdot 2CH_2Cl_2$ [14]. Distances of the Ru atoms to the centroids (CT) of the C_6Me_6 groups in the present complex are 1.861(2) and 1.845(2) Å and Re–Ru–CT angles are 179.1(12) and 179.1(9)°, for molecules A and B, respectively. The rings in A and B are inclined by 2.3 and 4.1° with respect to the Ru–Re line (see 'Supplementary material'). The methyl groups are off the mean plane of the benzene ring, pointing away from the Ru atom.

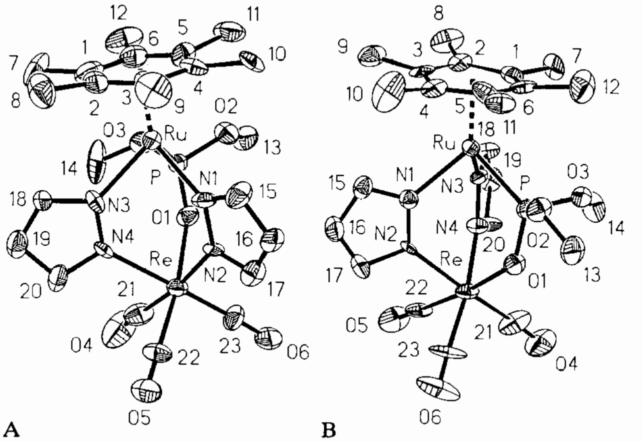


Fig. 1. Molecular structure of the two independent molecules of the complex, with 40% probability thermal ellipsoids, showing atom labelling scheme (H atoms omitted).

This situation is similar to that found for the C_5Me_5 group in $[\{C_5Me_5Rh\}_2(\mu\text{-}Pz)_2(\mu\text{-}PPh_2)]BF_4$ [15].

The Re atoms exhibit a distorted octahedral geometry. Bonds and angles involving the terminal carbonyl groups compare well with those reported for the related hydrotris(1-pyrazol-1-yl)borate derivative $HB(C_3H_3N_2)_3Re(CO)_3$ [16]. The two pyrazolate ligands in the present complex are essentially planar with normal bonds and angles. The other bridging ligand, the phosphonate group, coordinates to ruthenium via the phosphorus atom and to rhenium via the oxygen atom. The phosphoryl bond distance P–O(1) = 1.48(2) Å in molecule A is somewhat smaller than the P=O bonds reported for similar phosphonate bridged binuclear complexes [7b, 14, 17]. This value is indicative of the remaining partial double-bond character. The $P\text{–}OCH_3$ distances and $P\text{–}O\text{–}CH_3$ angles, on the other hand, vary within the usual range [18]. The relative orientations of the three bridging groups, as viewed along the Ru–Re line, are illustrated in the drawing shown in Fig. 2. Angles indicated on the Figure correspond to dihedral angles between least-squares planes of the bridging groups.

Cohesion on the structure seems to be achieved by van der Waals forces. Molecules in the crystal pack with the Ru–Ru axes roughly parallel to each other. There are some close lateral contacts between neighboring molecules and some head-to-tail contacts between terminal carbonyl groups and the hexamethylbenzene groups of equivalent molecules displaced along the *b* axis of the crystal.

Supplementary material

List of observed and calculated structure factors (11 pages), anisotropic thermal parameters, H atom coordinates, full list of bond angles, mean lines, planes and dihedral angles (9 pages) are available from the author (D.B.) on request.

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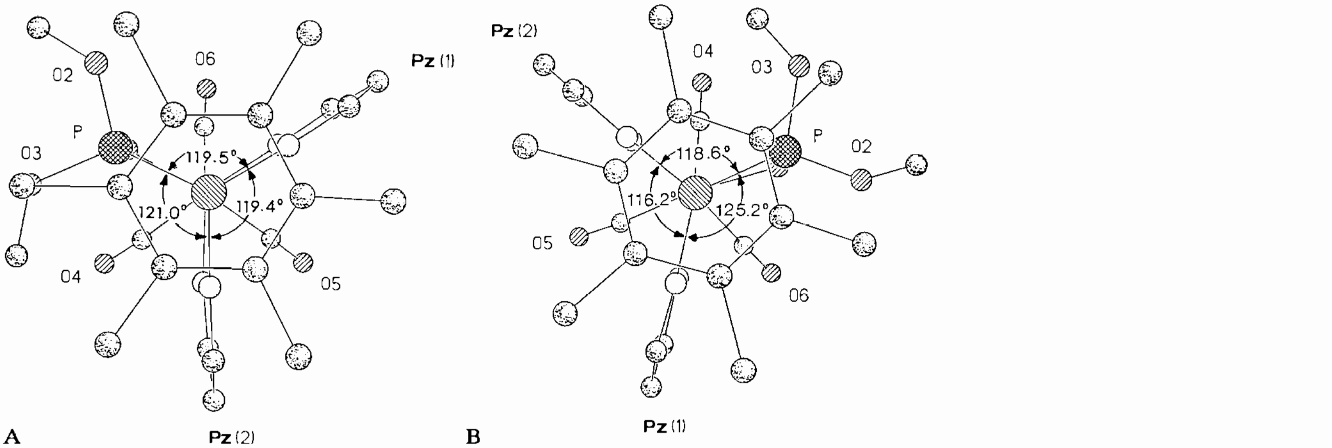

Fig. 2. Top view, along the Ru–Re vector, of the two independent molecules, showing the relative orientation of the bridging pyrazolates and phosphonate groups in the complex.

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