The addition of protons and metallic electrophiles to the electron-rich Ru–Ru bond of $[Ru_2(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]$. X-ray structure of $[Ru_2(\mu\text{-}AgPPh_3)(\mu\text{-}dan)(CO)_4(P^iPr_3)_2][BF_4]\cdot CH_2Cl_2$ (dan = 1,8-diamidonaphthalene)

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Abstract

The ruthenium(I) complex $[Ru_2(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]$ (**1**) (dan = 1,8-diamidonaphthalene) reacts with $HBF_4\cdot OEt_2$, $[AuCl(PPh_3)]/TlPF_6$ and $AgBF_4/PPh_3$ to give the cationic complexes $[Ru_2(\mu\text{-}M)(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]^+$ (M = H (**2**), AuPPh$_3$ (**3**), AgPPh$_3$ (**4**)), while the reactions with $[AuCl(tht)]$ (tht = tetrahydrothiophene) and AgO_2CCF_3 give the neutral derivatives $[Ru_2(\mu\text{-}M)(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]$ (M = AuCl (**5**), AgO_2CCF_3 (**6**)). Complex **1** also reacts with $SnCl_2$ to give $[Ru_2(\mu\text{-}SnCl_2)(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]$ (**7**), but in solution it dissociates $SnCl_2$ unless a large excess of the latter is present. In all cases, the added electrophiles symmetrically bridge the Ru–Ru bond of complex **1**, as indicated by IR and NMR spectroscopies. The structure of complex **4** has been confirmed by X-ray diffraction methods.

Introduction

In recent papers we have described the synthesis [1, 2] and some reactivity [2] of the binuclear ruthenium(I) dimer $[Ru_2(\mu\text{-}dan)(CO)_6]$. The X-ray crystal structures of $[Ru_2(\mu\text{-}dan)(CO)_4(L)_2]$ (L = $P(OPh)_3$, PPh$_3$) have revealed very short Ru–Ru distances (2.571(1) and 2.579(1) Å, respectively) [2, 3], suggesting that the close proximity of the metal atoms is imposed by the bridging ligand rather than by the electronic environment of each Ru atom, since other binuclear ruthenium(I) complexes present longer Ru–Ru distances [4].

The complex $[Ru_2(\mu\text{-}dmpz)_2(CO)_6]$ (dmpz = 3,5-dimethylpyrazolate), which has a longer Ru–Ru distance than the above mentioned complexes, 2.705(2) Å, does not react with sulfuric acid or with the metallic fragments $[MPPh_3]^+$ (M = Ag, Au) [4]. Interestingly, although the complex $[Ru_2(\mu\text{-}dan)(CO)_6]$ reacts with protonic acids, it does not react with metallic fragments [2]. However, the analogous compound $[Ru_2(\mu\text{-}dab)(CO)_4(PPh_3)_2]$ (dab = 1,2-diamidobenzene), which presents a Ru–Ru distance of

2.560(1) Å, does react with a variety of metallic electrophiles [5].

Since these data seemed to point out that the Ru–Ru bond of $[Ru_2(\mu\text{-}dan)(CO)_6]$ is not electron rich enough to react with metal electrophiles, we thought it was of interest to investigate the reactions of these reagents with the complex $[Ru_2(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]$ (**1**), in which the presence of triisopropylphosphine should increase the basic character of the Ru–Ru bond.
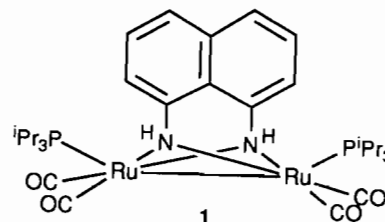
Results and discussion

Complex **1** was easily protonated with $HBF_4\cdot OEt_2$ in dichloromethane to give $[Ru_2(\mu\text{-}H)(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]BF_4$ (**2**). Analogously, complex **1** also reacted

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with the metallic fragments [AuPPh₃]⁺ and [Ag-PPh₃]⁺ (prepared *in situ* from [AuCl(PPh₃)] and TlPF₆ or from AgBF₄ and PPh₃, respectively) rendering the cationic complexes [Ru₂(μ-M)(μ-dan)(CO)₄(PⁱPr₃)₂]⁺ (M = AuPPh₃ (3), AgPPh₃ (4)). The three compounds 2–4 are isostructural, having the electrophilic fragments symmetrically bridging the Ru–Ru bonds, as shown by their IR (Table 1) and NMR (Table 2) spectra, which indicated a C_{2v} symmetry. Thus, their IR spectra displayed three ν(CO) absorptions shifted to higher wavenumbers

than those of complex 1 [2], suggesting a decrease of electron density at the Ru atoms. The ¹H NMR spectrum of complex 2 showed the hydride as a triplet due to coupling to two equivalent PⁱPr₃ ligands. The ³¹P {¹H} NMR spectrum of complex 2 was a singlet, and that of complex 3 an AX₂ spin system. The ³¹P {¹H} NMR spectrum of complex 4 was more complicated due to coupling of the three phosphorous atoms to ¹⁰⁷Ag and ¹⁰⁹Ag ($I = 1/2$), displaying a doublet of doublets for the PⁱPr₃ ligands and a doublet of broad multiplets for the PPh₃ ligand. The structure

TABLE 1. Analytical and IR data for compounds 2–7

Compound	Analysis (%)ᵃ			IR (cm⁻¹)	
	C	H	N	ν(CO)	ν(NH)ᵇ
2ᶜ	43.2	6.1	3.4	2057s, 2039m, 1991sᵈ	3300s
	(43.7)	(5.9)	(3.2)		
3ᵉ	43.5	4.7	1.9	2010s, 1991m, 1965sᵈ	3326m
	(43.1)	(4.7)	(2.0)		
4ᶜ	48.3	5.2	2.0	2000m, 1978m, 1933sᵈ	3313m
	(48.1)	(5.3)	(2.2)		
5	37.3	4.9	2.8	2011m, 1993m, 1946sᵈ	3340w
	(37.6)	(4.9)	(2.7)		
6ᶠ	37.8	4.6	2.4	1993s, 1982m, 1941mᵈ	3310w
	(38.3)	(4.8)	(2.5)		
7ᵍ				2057s, 2033m, 1987sʰ	3265m

ᵃCalculated values in parentheses. ᵇNujol mulls. ᶜBF₄ salt. ᵈIn CH₂Cl₂. ᵉPF₆ salt. ᶠCH₂Cl₂ solvate. ᵍThis compound was always contaminated with some SnCl₂ (see text). ʰIn THF.

TABLE 2. ¹H and ³¹P {¹H} NMR data for compounds 2–7 (δ, ppm)ᵃ

| Compound	¹H				³¹P {¹H}
	dan rings	NH	PⁱPr₃	other	
2ᵇ	7.58(d)	4.55(s)	1.26(m)	−10.13(t, 39ᶜ)	58.2(s)
	7.24(m)		0.99(dd)		
3ᵈ	ᵉ	4.30(s)	1.24(m)	7.7–7.1(m)	55.8(t, 40ᶠ)
			0.96(dd)		53.1(d, 40ᶠ)
4ᵈ	ᵉ	4.64(s)	1.22(m)	7.7–7.1(m)	48.6(dd, 42ᶠ, 28ᵍ)
			0.95(dd)		14.3(dm, 464ʰ)
5ᵇ	7.44(d)	3.81(s)	1.36(m)		53.1(s)
	7.11(t)		0.99(dd)		
	6.92(d)				
6ᵈ	7.50(d)	4.11(s)	1.36(m)		50.4(d, 37ᵍ)
	7.16(t)		0.98(dd)		
	6.99(d)				
7ᵈ	7.54(d)	3.75(s)	1.25(m)		58.7(sⁱ)
	7.50(d)		1.00(dd)		
	7.26(t)				

ᵃMultiplicity and coupling constants (Hz) in parentheses: the couplings between the naphthalene protons range from 7.3 to 7.7 Hz; complexes 2 and 4 are BF₄ salts, complex 3 is a PF₆ salt. ᵇIn CD₂Cl₂. ᶜ ²J(P–H). ᵈIn CDCl₃. ᵉThe resonances of the naphthalene protons overlap with those of the PPh₃ ligand. ᶠ ³J(P–P). ᵍ ²J(P–¹⁰⁷Ag) ≈ ²J(P–¹⁰⁹Ag). ʰ ¹J(P–¹⁰⁷Ag) ≈ ¹J(P–¹⁰⁹Ag). ⁱWith tin satellites, ²J(P–¹¹⁷Sn) ≈ ²J(P–¹¹⁹Sn) ≈ 37 Hz.

of complex **4** has been confirmed by a single crystal X-ray diffraction study (see Fig. 1) which is discussed below.

	M
2	H
3	AuPPh$_3$
4	AgPPh$_3$
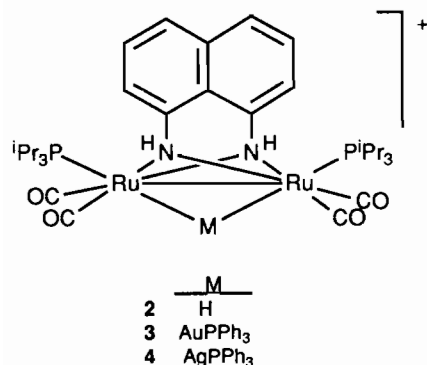
Complex **1** did not react with the [CuPPh$_3$]$^+$ fragment (prepared *in situ* from [Cu$_4$Cl$_4$(PPh$_3$)$_4$] and TlPF$_6$). This result is not surprising, since molecular orbital calculations have revealed that the fragments [MPPh$_3$]$^+$ (M = Cu, Ag, Au) are not quite isolobal [6]. In fact, the complex [Rh$_2$Cp$_2$(μ-CO)(μ-dppm)] (dppm = bis(diphenylphosphino)methane) reacts with [AuPPh$_3$]$^+$ but not with [CuPPh$_3$]$^+$ or [Ag-PPh$_3$]$^+$ [7]. It is also known [8] that the complexes [Rh$_2$(μ-MPPh$_3$)(μ-dan)(CO)$_2$(PPh$_3$)$_2$]$^+$ (M = Cu, Ag, Au) can be prepared by reaction of [Rh$_2$(μ-dan)(CO)$_2$(PPh$_3$)$_2$] with the corresponding group 11 metal fragments, although in this case the initial rhodium compound is a 32-electron complex for which no Rh–Rh bond has to be assumed. However, compound **1** is a 34-electron complex and a Ru–Ru bond is required to account for its diamagnetism.

Complex **1** also remained unaltered upon treatment with a large excess of MeO$_3$SCF$_3$ in dichloromethane. However, it has been reported that the Ru–Ru bond of the ruthenium(0) dimer [Ru$_2$(μ-dmpm)$_2$(μ-CO)(CO)$_4$] (dmpm = bis(dimethylphosphino)-methane) can be methylated with that reagent [9].

	M
5	AuCl
6	AgO$_2$CCF$_3$
7	SnCl$_2$
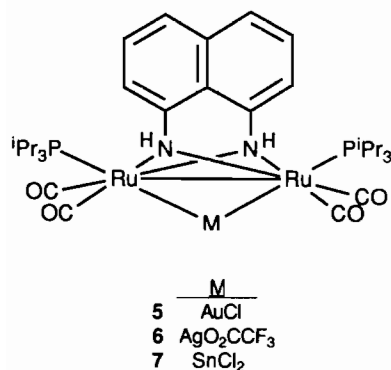
The neutral complexes [Ru$_2$(μ-M)(μ-dan)-(CO)$_4$(P^{i}Pr$_3$)$_2$] (M = AuCl (**5**), AgO$_2$CCF$_3$ (**6**)) were prepared by reacting equimolecular amounts of com-

plex **1** and [AuCl(tht)] (tht = tetrahydrothiophene) or AgO$_2$CCF$_3$. Again, their IR spectra (Table 1) showed three ν(CO) bands shifted to higher wavenumbers than those of the parent compound, and their ^{31}P {^{1}H} NMR spectra (Table 2) indicated equivalent P^{i}Pr$_3$ ligands, as expected for a triangular arrangement of the metal atoms. The IR spectrum of complex **6** also showed that the trifluoroacetate ligand chelates the silver atom through both oxygens [10], displaying the ν_{asym}(CO$_2$) and ν_{sym}(CO$_2$) at 1684 and 1462 cm^{-1}, respectively. This type of coordination has also been observed by X-ray diffraction in the trifluoroacetato complex [Rh$_2$Cp$_2$(μ-AgO$_2$CCF$_3$)(μ-CO)(μ-dppm)] [7].

Treatment of complex **1** with SnCl$_2$ in THF gave [Ru$_2$(μ-SnCl$_2$)(μ-dan)(CO)$_4$(P^{i}Pr$_3$)$_2$] (**7**), but IR monitoring of the reaction established that a large excess of SnCl$_2$ (over twenty-fold) is necessary to complete the reaction. In fact, all the attempts to isolate pure complex **7** were unsuccessful, since complex **1** was reformed as soon as the excess of SnCl$_2$ was removed. Thus, the spectroscopic data shown in Tables 1 and 2 for this complex correspond to a mixture of **7** and SnCl$_2$. These data also suggest that the SnCl$_2$ fragment symmetrically bridges the Ru–Ru bond.

Finally, we think it is worth noting that complex **1** remained unaltered upon treatment with PbCl$_2$, SO$_2$, CH$_2$N$_2$, [Rh$_2$Cl$_2$(cod)$_2$] (cod = 1,5-cyclooctadiene), [Rh(cod)(THF)$_2$]$^+$ and SnClMe$_3$/TlPF$_6$ (as well as with the above cited [CuPPh$_3$]$^+$ and MeO$_3$SCF$_3$) and that although it reacted with [Rh$_2$Cl$_2$(CO)$_4$], (NO)BF$_4$, [Au(C$_6$F$_5$)(tht)] and I$_2$, it gave mixtures of compounds which we have been unable to separate and characterize.

Description of the structure of complex 4

The crystal studied by X-ray diffraction consisted of cationic complexes [Ru$_2$(μ-AgPPh$_3$)(μ-dan)-(CO)$_4$(P^{i}Pr$_3$)$_2$]$^+$, BF$_4^-$ anions and dichloromethane molecules of crystallization. A diagram of the cation is depicted in Fig. 1, fractional atomic coordinates are given in Table 3, and selected bond lengths and angles are listed in Table 4.

The structure shows an AgPPh$_3$ fragment attached to both Ru atoms of complex **1**. The Ru–Ag distances, 2.788(2) and 2.780(2) Å, are comparable to those found in the cluster [Ru$_3$(μ-AgPPh$_3$)(μ_3-PPh-CH$_2$PPh$_2$)(CO)$_9$] [11], 2.806(1) and 2.767(1) Å. As expected, the Ru–Ru distance, 2.699(2) Å, is longer than those found in [Ru$_2$(μ-dan)(CO)$_4$(L)$_2$], 2.571(1) (L = P(OPh)$_3$) [2] and 2.579(1) Å (L = PPh$_3$) [3], but it is still within the bonding range: the Ru–Ru distances in [Ru$_3$(CO)$_{12}$] average 2.854(1) Å [12]. The Ag(1)–P(1) vector does not point to the center
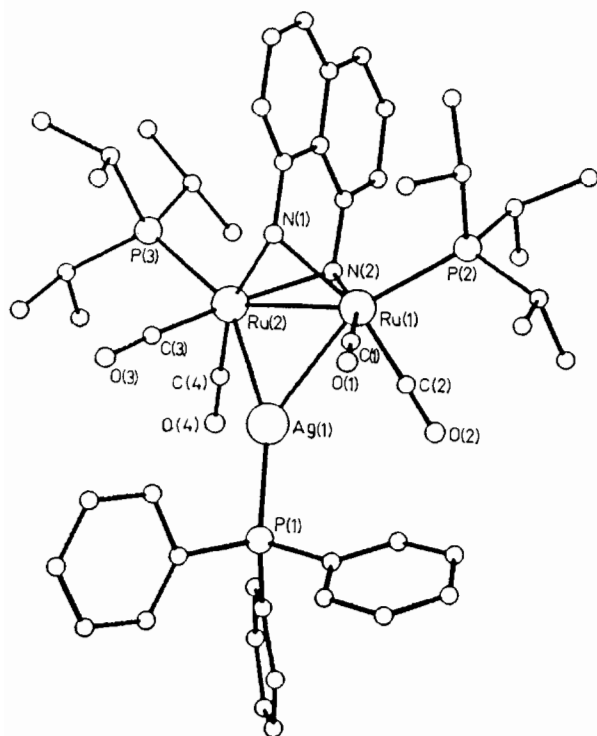
Fig. 1. PLUTO drawing of the cation $[Ru_2(\mu\text{-}AgPPh_3)(\mu\text{-}dan)(CO)_4(P^iPr_3)_2]^+$, with the atomic numbering scheme.

of the Ru–Ru bond, since the Ru(1)–Ag(1)–P(1) and Ru(2)–Ag(1)–P(1) angles are rather different, 142.2(1) and 159.7(1)°.

The structure of the complex without the AgPPh$_3$ fragment resembles those of $[Ru_2(\mu\text{-}dan)(CO)_4(L)_2]$ (L = P(OPh)$_3$, PPh$_3$) [2, 3], the only remarkable difference being the wider Ru–N–Ru angles, 72.9(5) and 72.6(5)°, as a consequence of the longer Ru–Ru distance.

Experimental

Unless otherwise noted, all reactions were carried out under nitrogen, at room temperature, using standard Schlenk techniques. Solvents were dried and distilled prior to use. The following chemicals were prepared according to literature methods: complex 1 [2], [AuCl(tht)] [13], [AuCl(PPh$_3$)] [14], [Cu$_4$Cl$_4$(PPh$_3$)$_4$] [15], AgO$_2$CCF$_3$ [16], [Au(C$_6$F$_5$)-(tht)] [13], [Rh$_2$Cl$_2$(cod)$_2$] [17] and [Rh$_2$Cl$_2$-(CO)$_4$] [18]; all other reagents were obtained from Aldrich. Elemental analyses were obtained with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer FT 1720-X spectro-photometer. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AC-300 instrument at 23 °C with SiMe$_4$

TABLE 3. Fractional atomic coordinates for complex 4 with e.s.d.s in parentheses

Atom	x	y	z
Ag(1)	0.2700(1)	0.19687(9)	0.17526(6)
Ru(1)	0.3285(1)	0.18858(9)	0.30570(6)
Ru(2)	0.1488(1)	0.23209(8)	0.24966(6)
C(1)	0.363(1)	0.104(1)	0.2679(8)
O(1)	0.385(1)	0.0510(8)	0.2454(7)
C(2)	0.413(1)	0.250(1)	0.2783(8)
O(2)	0.4620(9)	0.2882(7)	0.2606(6)
C(3)	0.085(1)	0.173(1)	0.1823(8)
O(3)	0.0462(9)	0.1381(7)	0.1387(5)
C(4)	0.149(1)	0.313(1)	0.1991(8)
O(4)	0.1502(9)	0.3624(8)	0.1663(6)
P(1)	0.3244(3)	0.1767(3)	0.0827(2)
C(5)	0.336(1)	0.262(1)	0.0423(8)
C(6)	0.296(1)	0.325(1)	0.0600(9)
C(7)	0.303(1)	0.390(1)	0.029(1)
C(8)	0.347(2)	0.393(1)	−0.018(1)
C(9)	0.389(1)	0.334(1)	−0.0346(8)
C(10)	0.387(1)	0.266(1)	−0.0049(8)
C(11)	0.442(1)	0.135(1)	0.0980(9)
C(12)	0.467(2)	0.081(1)	0.062(1)
C(13)	0.561(2)	0.056(1)	0.075(1)
C(14)	0.625(2)	0.078(2)	0.125(2)
C(15)	0.599(2)	0.130(2)	0.162(1)
C(16)	0.510(2)	0.157(2)	0.149(1)
C(17)	0.249(1)	0.118(1)	0.0256(9)
C(18)	0.236(1)	0.117(1)	−0.0387(9)
C(19)	0.178(2)	0.069(1)	−0.078(1)
C(20)	0.125(2)	0.019(1)	−0.052(1)
C(21)	0.134(2)	0.016(1)	0.012(1)
C(22)	0.197(1)	0.066(1)	0.053(1)
P(2)	0.4479(3)	0.1623(3)	0.4025(2)
C(33)	0.429(1)	0.079(1)	0.4461(8)
C(34)	0.381(1)	0.0164(9)	0.4026(8)
C(35)	0.373(1)	0.093(1)	0.4968(8)
C(36)	0.465(1)	0.236(1)	0.4628(8)
C(37)	0.551(1)	0.224(1)	0.5210(7)
C(38)	0.475(1)	0.313(1)	0.4370(9)
C(39)	0.572(1)	0.144(1)	0.3975(8)
C(40)	0.586(1)	0.075(1)	0.364(1)
C(41)	0.620(1)	0.207(1)	0.371(1)
P(3)	−0.0037(3)	0.2669(3)	0.2680(2)
C(42)	0.008(1)	0.335(1)	0.3319(8)
C(43)	0.063(1)	0.405(1)	0.3225(9)
C(44)	−0.083(1)	0.355(1)	0.3505(9)
C(45)	−0.062(1)	0.187(1)	0.2966(8)
C(46)	−0.171(1)	0.197(1)	0.290(1)
C(47)	−0.049(2)	0.116(1)	0.266(1)
C(48)	−0.099(1)	0.305(1)	0.2010(8)
C(49)	−0.124(2)	0.254(1)	0.1455(9)
C(50)	−0.081(1)	0.380(1)	0.1816(9)
N(1)	0.195(1)	0.1453(7)	0.3146(6)
N(2)	0.251(1)	0.2771(8)	0.3296(6)
C(23)	0.172(1)	0.146(1)	0.3732(8)
C(24)	0.134(1)	0.088(1)	0.3961(8)
C(25)	0.113(1)	0.089(1)	0.4539(8)
C(26)	0.127(1)	0.152(1)	0.4894(9)
C(27)	0.164(1)	0.215(1)	0.4697(8)

(continued)

TABLE 3 (*continued*)

Atom	x	y	z
C(28)	0.191(1)	0.2132(9)	0.4100(7)
C(29)	0.229(1)	0.277(1)	0.3883(7)
C(30)	0.243(1)	0.338(1)	0.4254(9)
C(31)	0.216(1)	0.340(1)	0.4821(9)
C(32)	0.177(1)	0.281(1)	0.5025(8)
B(1)	0.872(2)	0.039(2)	0.782(2)
F(1)	0.828(1)	0.0908(9)	0.7951(9)
F(2)	0.970(1)	0.0388(8)	0.8018(7)
F(3)	0.831(1)	−0.0275(8)	0.7809(9)
F(4)	0.862(1)	0.044(1)	0.716(1)
C(60)	0.051(2)	0.104(2)	0.676(2)
Cl(1)	0.0743(9)	0.0513(7)	0.6251(5)
Cl(2)	0.152(1)	0.147(1)	0.7179(8)

TABLE 4. Selected bond lengths (Å) and angles (°) in complex **4**

Ru(1)–Ru(2)	2.698(2)	Ru(1)–N(2)	2.12(1)
Ag(1)–Ru(1)	2.779(2)	Ru(2)–N(1)	2.13(1)
Ag(1)–Ru(2)	2.780(2)	Ru(2)–N(2)	2.14(1)
Ag(1)–P(1)	2.403(5)	Ru(1)–C(1)	1.89(2)
Ru(1)–P(2)	2.417(5)	Ru(1)–C(2)	1.88(2)
Ru(2)–P(3)	2.440(5)	Ru(2)–C(3)	1.88(2)
Ru(1)–N(1)	2.15(1)	Ru(2)–C(4)	1.86(2)
Ru(1)–Ag(1)–Ru(2)	58.1(1)	Ru(1)–N(1)–Ru(2)	78.3(4)
Ag(1)–Ru(1)–Ru(2)	61.0(1)	Ru(1)–N(2)–Ru(2)	78.5(5)
Ag(1)–Ru(2)–Ru(1)	60.9(1)	N(1)–Ru(1)–N(2)	73.0(5)
Ru(1)–Ag(1)–P(1)	142.3(1)	N(1)–Ru(2)–N(2)	72.9(5)
Ru(2)–Ag(1)–P(1)	159.7(1)	N(1)–Ru(1)–C(2)	158.7(7)
Ag(1)–Ru(1)–P(2)	151.2(1)	N(1)–Ru(2)–C(4)	162.1(7)
Ag(1)–Ru(2)–P(3)	154.5(1)	N(2)–Ru(1)–C(1)	163.4(7)
Ru(1)–Ru(2)–P(3)	144.4(1)	N(2)–Ru(2)–C(3)	164.6(6)
Ru(2)–Ru(1)–P(2)	147.8(1)		

(internal, ^{1}H) or 85% H_3PO_4 (external, ^{31}P) as references ($\delta = 0$ ppm).

[Ru$_2$(μ-H)(μ-dan)(CO)$_4$(P^iPr_3)$_2$]BF$_4$ (2)

An excess of HBF$_4$·OEt$_2$ (0.05 ml) was added to a solution of complex **1** (50 mg, 0.063 mmol) in dichloromethane (5 ml). The reaction was instantaneous (IR). The solution was evaporated to dryness and the residue washed with three 5 ml portions of diethyl ether to give a yellow solid (37 mg, 75%).

[Ru$_2$(μ-AuPPh$_3$)(μ-dan)(CO)$_4$(P^iPr_3)$_2$]PF$_6$ (3)

A mixture of complex **1** (40 mg, 0.056 mmol), [AuCl(PPh$_3$)] (28 mg, 0.056 mmol) and TlPF$_6$ (30 mg, 0.086 mmol) in THF (15 ml) was stirred for 1 h and then evaporated to dryness. The residue was extracted with dichloromethane (2×5 ml) and filtered under nitrogen to remove TlCl and the excess of TlPF$_6$. The solution was evaporated to dryness and

the residue washed with two 3 ml portions of diethyl ether to give a yellow solid (44 mg, 56%).

[Ru$_2$(μ-AgPPh$_3$)(μ-dan)(CO)$_4$(P^iPr_3)$_2$]BF$_4$ (4)

Complex **1** (40 mg, 0.056 mmol) was added to a solution of AgBF$_4$ (11 mg, 0.056 mmol) and PPh$_3$ (15 mg, 0.056 mmol) in THF (5 ml). The solution, which was protected from light with a black plastic film, was evaporated to dryness and the residue washed with 3 ml of diethyl ether to give a golden-yellow solid (50 mg, 72%).

[Ru$_2$(μ-AuCl)(μ-dan)(CO)$_4$(P^iPr_3)$_2$] (5)

Complex **1** (30 mg, 0.038 mmol) and [AuCl(tht)] (12 mg, 0.038 mmol) were stirred in dichloromethane (5 ml) for 10 min. At this point, a small amount of metallic gold was observed on the Schlenk tube walls. The solution was filtered under nitrogen and evaporated to dryness. The residue was washed with three 3 ml portions of diethyl ether to give a greenish yellow solid (15 mg, 39%).

[Ru$_2$(μ-AgO$_2$CCF$_3$)(μ-dan)(CO)$_4$(P^iPr_3)$_2$] (6)

Complex **1** (40 mg, 0.056 mmol) and AgO$_2$CCF$_3$ (13 mg, 0.059 mmol) were stirred in dichloromethane (5 ml) for 10 min with the Schlenk tube protected from light with a black plastic film. The resulting solution was evaporated to dryness and the residue washed with three 5 ml portions of diethyl ether to give the dichloromethane solvate **6**·CH$_2$Cl$_2$ as a greenish yellow solid (15 mg, 24%).

[Ru$_2$(μ-SnCl$_2$)(μ-dan)(CO)$_4$(P^iPr_3)$_2$] (7)

A solution of complex **1** (40 mg, 0.056 mmol) and SnCl$_2$ (13 mg, 0.069 mmol) in THF (10 ml) was stirred at room temperature for 45 min. After this time, the IR spectrum of the solution showed no reaction. After 1 h of stirring at reflux temperature the IR spectrum showed a small amount of the new compound. Several portions of SnCl$_2$ were progressively added, while the solution was maintained at reflux temperature, until the IR spectrum showed complete conversion of complex **1** into complex **7**. The total amount of SnCl$_2$ added was 240 mg (1.26 mmol). All the attempts to isolate complex **7** free of SnCl$_2$ resulted in mixtures of complexes **7** and **1**.

Crystal structure determination of complex 4

Crystal data. C$_{50}$H$_{65}$AgBF$_4$N$_2$O$_4$P$_3$Ru$_2$·CH$_2$Cl$_2$, $M = 1332.74$, monoclinic, space group $P2_1/n$, $a = 14.530(5)$, $b = 18.321(6)$, $c = 22.040(9)$ Å, $\beta = 105.28(2)°$, $V = 5659(4)$ Å^3, $Z = 4$, $D_c = 1.56$ g cm^{-3}. Mo Kα radiation, graphite monochromator, $\lambda =$

0.71073 Å, μ(Mo Kα) = 10.90 cm^{-1}, $F(000)$ = 2696, T = 200 K.

A greenish yellow crystal of dimensions $0.23 \times 0.17 \times 0.10$ mm, grown from dichloromethane–diethylether, was selected. The data were collected on an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions were determined from the angular settings of 25 reflections with $15 < \theta < 20°$. Space group $P2_1/n$ from systematic absences. 10629 reflections measured, (h,k,l) range (-17, 0, 0) to 16, 21, 26), $0° < \theta < 25°$, ω–2θ scan technique, maximum scan time 60 s per reflection. Intensity checked by monitoring three standard reflections every 60 min. Final drift correction factors between 0.99 and 1.07. Profile analysis [19] was performed on all reflections. Some double measured reflections averaged, $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I = 0.090$; 9853 unique reflections and 3383 observed with $I > 3\sigma(I)$. Lorentz and polarization corrections applied and data reduced to $|F_o|$ values. The structure was solved by Patterson interpretation, using SHELX86 [20]. Isotropic least-squares refinement, using a version of SHELX [21] modified by the authors, converged to $R = 0.09$. Further empirical absorption correction [22] gave $R = 0.07$ (max. and min. factors 1.19 and 0.78). Anisotropic refinements followed by a difference Fourier synthesis allowed the location of most of the hydrogen atoms.

Except Cl(2), which was isotropically refined, the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were left riding on their parent atoms at 1.080 Å and refined isotropically with a common thermal parameter. Final $R = 0.055$, $R_w = 0.054$ for the 3383 observed reflections and 666 variables. Function minimized $\Sigma w(F_o - F_c)^2$, $w = 1/(\sigma^2(F_o) + 0.0004F_o^2)$, with $\sigma(F_o)$ from counting statistics. Maximum shift over error ratio in the last full-matrix least-squares cycle less than 0.04. The final difference Fourier map showed two peaks of 1.73 and 1.50 e/Å^3 near the isotropic Cl(2) atom of the disordered dichloromethane molecule. The rest of the peaks were no higher than 0.88 e/Å^3 nor lower than -0.82 e/Å^3. Atomic scatering factors were taken from the International Tables [23]. Tables 3 and 4 list the atomic coordinates and selected bond distances and angles. See also 'Supplementary material'.

Supplementary material

Tables of fractional atomic coordinates (including H atoms), complete bond distances and angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. A table of structure factors is available from the authors on request.

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