

Derivative Chemistry of $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_6]$, a Binuclear Ruthenium(I) Carbonyl Complex Containing a Bridging Benzene-1,2-dithiolate Ligand

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The known dithiolate-bridged ruthenium(I) complex $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_6]$ (**1**) (bdt = benzene-1,2-dithiolate) has been prepared in fair yield (55%) by the sequential treatment of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ with carbon monoxide, benzene-1,2-dithiol and zinc in a one-pot reaction. Complex **1** reacts readily with monodentate phosphanes to give, stepwise, the penta- and tetracarbonyl derivatives $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_{6-n}(\text{PR}_3)_n]$ ($n = 1, 2$; $\text{R} = \text{Ph}, \text{Cy}, i\text{Pr}$). However, the reaction of **1** with one equivalent of bis(diphenylphosphanyl)methane (dppm) affords a mixture of complex **1** and the disubstituted derivative $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\eta^1\text{-dppm})_2]$, in which the dppm ligands are monodentate. This mixture is subsequently transformed into a polymeric material of formula $[\{\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\mu\text{-dppm})\}_n]$, which consists of binuclear $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4]$ units linked to each other by bridging dppm ligands. The use of two equivalents of dppm leads to $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\eta^1\text{-dppm})_2]$ in quantitative yield. The X-ray diffraction structure of $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\text{P}i\text{Pr}_3)_2]$ (**3c**) confirms that the phosphane ligands are located in axial positions, *cis* to both sulfur atoms, and that the Ru–Ru distance is short [2.6753(7) Å]. A comparative study of the reactivity of complexes **1** and **3c** with the electrophiles H^+ , $[\text{Au}(\text{PPh}_3)]^+$, and HgCl_2 has allowed the isolation of the derivatives $[\text{Ru}_2(\mu\text{-H})(\mu\text{-bdt})(\text{CO})_{6-n}(\text{P}i\text{Pr}_3)_n][\text{BF}_4]$ ($n = 0, 2$), $[\text{Ru}_2\text{Au}(\mu\text{-bdt})(\text{CO})_{6-n}(\text{P}i\text{Pr}_3)_n(\text{PPh}_3)][\text{BF}_4]$ ($n = 0, 2$) and $[\text{Ru}_2\text{HgCl}_2(\mu\text{-bdt})(\text{CO})_{6-n}(\text{P}i\text{Pr}_3)_n]$ ($n = 0, 2$), respectively.

Introduction

Over the past few years, several authors have reported general high-yield routes to binuclear ruthenium(I) tetracarbonyl complexes containing two bridging alkyl- or arylthiolate ligands of the type $[\text{Ru}_2(\mu\text{-SR})_2(\text{CO})_4(\text{PR}_3)_2]$ ^[1–4]. However, the closely related hexacarbonyl compounds $[\text{Ru}_2(\mu\text{-SR})_2(\text{CO})_6]$, although known for many years, have so far been prepared in low yields^[5–11], their derivative chemistry being virtually unexplored.

We now report a new synthesis of the hexacarbonyl complex $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_6]$ (**1**) (bdt = benzene-1,2-dithiolate), starting from readily accessible starting materials ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, benzene-1,2-dithiol, carbon monoxide, and zinc), in a fair yield (50–60%), following a simple one-pot reaction which can be carried out on milligram or gram scales.

Such a convenient synthetic procedure, in addition to the fact that the doubly bridging attachment of the bdt ligand to the metal atoms in complex **1** rules out the complication of having *syn* and *anti* isomers, which do exist in bis(monothiolate)-bridged complexes^[4], makes complex **1** an excellent candidate for reactivity studies. We report herein its reactivity with some nucleophilic and electrophilic reagents. This type of reactivity study has not been previously reported on hexacarbonyl thiolate-bridged diruthenium(I)

complexes, probably as a consequence of the lack of a convenient synthetic route to such compounds.

Results and Discussion

Synthesis of Complex 1

The reaction of carbon monoxide with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in 2-methoxyethanol at reflux temperature gives a yellow solution. Treatment of this solution with benzene-1,2-dithiol and granular zinc as reducing agent has allowed the isolation of the hexacarbonyl complex **1** in 55% yield. This complex has previously been prepared in lower yield (35%) by treating $[\text{Ru}_3(\text{CO})_{12}]$ with benzene-1,2-dithiol in toluene at reflux temperature^[11].

An analogous synthetic method has previously been used to prepare other complexes containing ligand-bridged $\text{Ru}(\text{CO})_3$ units, such as $[\text{Ru}_2(\mu\text{-pz})_2(\text{CO})_6]$ (Hpz = pyrazole)^[12] and $[\text{Ru}_3(\mu\text{-PPh}_2)_3(\text{CO})_9]\text{Cl}$ ^[13]. It is well known that the yellow solution formed by treating $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ with carbon monoxide in 2-methoxy- or 2-ethoxyethanol is a useful precursor for the synthesis of mononuclear ruthenium(II) compounds^[14] and for the low-pressure preparation of $[\text{Ru}_3(\text{CO})_{12}]$ ^[15]; however, not until recently was the colorless ruthenium(II) dimer $[\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{CO})_6]$ described as the major component of that yellow solution^[16].

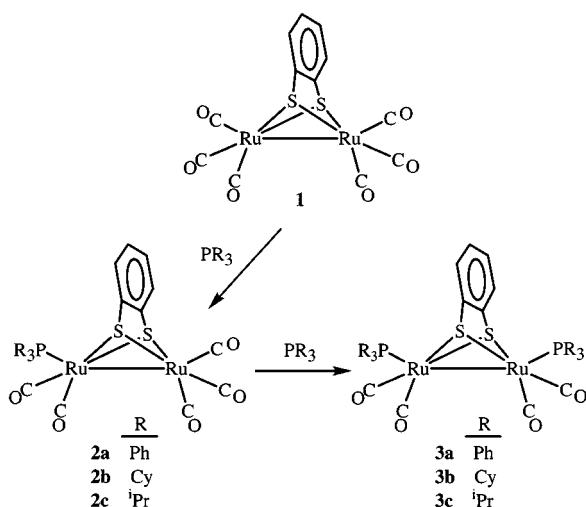
Reactions of Complex 1 with Monodentate Phosphane Ligands

Addition of one equivalent of a monodentate phosphane ligand to a room temperature THF solution of compound

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1 led to the quantitative (IR) formation of monosubstituted derivatives of the type $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_5(\text{PR}_3)]$ (**2a**: R = Ph; **2b**: R = Cy; **2c**: R = *i*Pr). The three compounds have very similar IR spectra in the carbonyl stretching region (Table 1), as expected for compounds having analogous structures. The structure depicted in Scheme 1 for these compounds, in which the phosphane ligand is in a position *cis* to both sulfur atoms, has been unequivocally inferred from their ^1H -NMR spectra, which show the aromatic protons of the bridging bdt ligand as two multiplets corresponding to an AA'MM' spin system; therefore, the phosphorus atom of the phosphane ligand is in a mirror plane that cuts the bdt ligand into two identical halves (C_s symmetry).



Scheme 1. Reactivity of complex **1** with monophosphanes

Table 1. Selected IR and NMR data

Comp	$\nu(\text{CO})^{[a]}$ [cm^{-1}]	$\delta(^3\text{P}\{^1\text{H}\})^{[b]}$ [ppm]
2a	2064 (s), 2009 (vs), 1985 (m), 1948 (w) ^[c]	40.6 (s)
2b	2059 (s), 2001 (vs), 1979 (m), 1937 (w) ^[c]	56.6 (s)
2c	2061 (s), 2002 (vs), 1981 (m), 1938 (w) ^[c]	64.2 (s)
3a	2013 (vs), 1978 (m), 1948 (s) ^[c]	37.4 (s)
3b	2002 (vs), 1986 (m), 1934 (s) ^[c]	48.7 (s)
3c	2007 (vs), 1964 (m), 1935 (s) ^[c]	57.8 (s)
4	2011 (vs), 1975 (m), 1945 (s) ^[c]	25.7 (m), −24.9 (m)
5	1997 (vs), 1967 (m), 1938 (s) ^[d]	
6b	2068 (vs), 2050 (m), 2010 (s) ^[c]	63.7 (s)
7a	2097 (vs), 2055 (s), 2040 (m) ^[c]	64.8 (s)
7b	2020 (w), 2002 (m), 1962 (vs) ^[c]	59.5 (d) ^[e] , 57.2 (t) ^[e]
8a	2119 (vs), 2069 (s), 2008 (w), 1985 (w) ^[f]	
8b	2049 (m), 2034 (m), 1995 (s) ^[c]	59.4 (s)

^[a] Abbreviations for IR data: s = strong, m = medium, w = weak, v = very. — ^[b] In CDCl_3 ; abbreviations for NMR data: s = singlet, d = doublet, t = triplet, m = multiplet. — ^[c] In CH_2Cl_2 . — ^[d] In Nujol mull. — ^[e] $J_{\text{P-P}} = 32.0$ Hz. — ^[f] In acetone.

Addition of at least two equivalents of a monodentate phosphane ligand to a room temperature THF solution of compound **1** led to the immediate formation of monosubstituted derivatives. The incorporation of a second phosphane ligand into the complexes required a higher tempera-

ture (THF under reflux), leading to the compounds $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\text{PR}_3)_2]$ (**3a**: R = Ph; **3b**: R = Cy; **3c**: R = *i*Pr). The structure of C_{2v} symmetry shown in Scheme 1 for these compounds is validated by their IR [three $\nu(\text{CO})$ absorptions] and NMR spectroscopic data (an AA'MM' spin system accompanied by the signals corresponding to the phosphane ligand in the ^1H -NMR spectrum and one singlet in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum), which are compatible with the existence in the compounds of two perpendicular mirror planes.

It has been reported that the binuclear ruthenium(I) complex $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_6]$ ($\text{H}_2\text{dan} = 1,8\text{-diaminonaphthalene}$), which is structurally related to **1** but has an *N*-donor instead of an *S*-donor bridging ligand, undergoes a rapid substitution of two CO ligands by phosphane ligands at room temperature^[17]. This has been associated with a strong *cis* labilization effect of the hard *N*-donor bridging ligand^[18]. The fact that the second substitution of CO by a phosphane ligand in **1** is slow indicates that the bdt ligand is not as strong *cis* labilizer as the dan ligand, probably due to the softer character of the *S*-donor ligand.

Compounds **3a**, **3b**, and **3c** could also be prepared in fair yields (43–73%) in one-pot reactions starting from $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, in an analogous procedure as that described above for compound **1** but carrying out the final step in the presence of the appropriate phosphane ligand. While this work was in progress, Shiu et al. reported an alternative synthesis of compound **3a** by treating the cationic binuclear compound $[\text{Ru}_2(\text{CO})_4(\text{PPh}_3)_2(\text{MeCN})_4][\text{BF}_4]_2$ with benzene-1,2-dithiol in the presence of triethyl amine^[3].

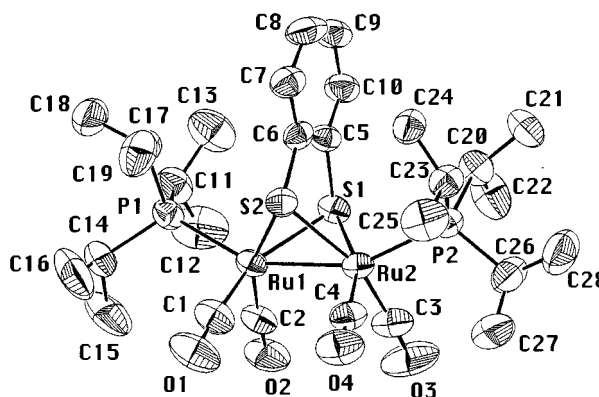


Figure 1. Molecular structure of complex **3c**. Thermal ellipsoids are drawn at 50% probability level

Compound **3c** has been characterized by X-ray diffraction methods (Figure 1). Relevant bond lengths and angles are given in Table 2. Overall, the structure reminds those of many other diruthenium(I) complexes containing bridging ligands^[2–4,11,18,19]. The most interesting feature is that the Ru–Ru distance [2.6753(7) Å] is comparable to that found in the unsubstituted complex **1** [2.650(2) Å]^[11] and also to those found in related complexes containing other thiolate bridging ligands^[2–4]. These data indicate that the metal–metal distance in diruthenium(I) compounds containing bridging ligands is little affected by the nature of the terminal ligands. However, such a distance is indeed affected

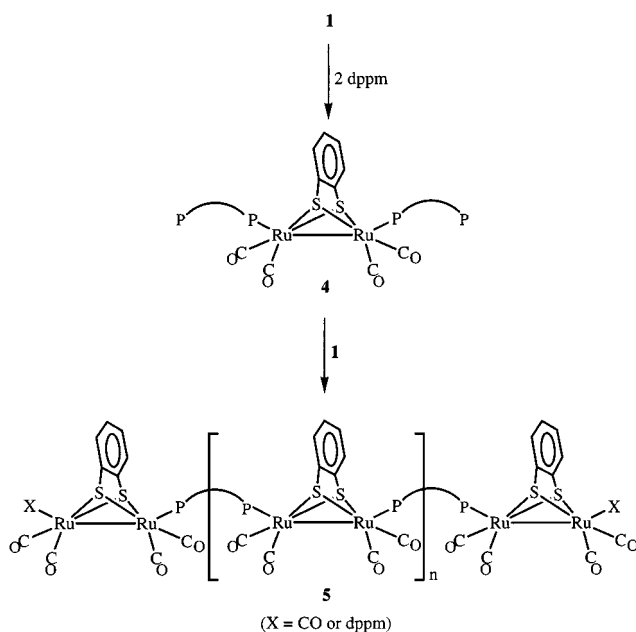
by the nature of the bridging ligands, since the shorter Ru–Ru distance found in the complex $[\text{Ru}_2(\mu\text{-dab})(\text{CO})_4(\text{PPh}_3)_2]$ ($\text{H}_2\text{dab} = 1,2\text{-diaminobenzene}$), 2.558(1) Å^[19], which is analogous to **3a** but has *N*-donor instead of *S*-donor atoms, can be associated to the smaller size of bridgehead nitrogen atom.

Table 2. Selected structural parameters in complex **3c**

Bond Lengths [Å]		Bond Angles [°]	
Ru(1)–Ru(2)	2.6753(7)	C(1)–Ru(1)–C(2)	89.4(3)
Ru(1)–S(1)	2.430(2)	C(1)–Ru(1)–S(1)	155.8(3)
Ru(1)–S(2)	2.428(2)	C(1)–Ru(1)–S(2)	93.2(2)
Ru(2)–S(1)	2.428(2)	C(2)–Ru(1)–S(1)	91.4(2)
Ru(2)–S(2)	2.434(2)	C(2)–Ru(1)–S(2)	157.1(2)
Ru(1)–P(1)	2.411(2)	S(1)–Ru(1)–Ru(2)	56.54(4)
Ru(2)–P(2)	2.400(2)	S(2)–Ru(1)–Ru(2)	56.73(4)
Ru(1)–C(1)	1.868(8)	S(1)–Ru(1)–S(2)	77.20(6)
Ru(1)–C(2)	1.862(7)	P(1)–Ru(1)–Ru(2)	153.30(4)
Ru(2)–C(3)	1.865(7)	P(1)–Ru(1)–S(1)	104.18(6)
Ru(2)–C(4)	1.858(9)		

Reactions of Complex **1** with the Bidentate Ligand dpmm

Treatment a THF solution of compound **1** with bis(diphenylphosphanyl)methane (dpmm), in a 1:1 mol ratio, readily resulted (30 min, room temperature) in the formation of the disubstituted derivative $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\eta^1\text{-dpmm})_2]$ (**4**), while half the initial amount of the starting complex **1** remained (IR identification). After stirring for 4 h, a yellow solid began to precipitate from the solution. After 3 days the precipitate was copious and the liquid phase was nearly colorless. This solid, subsequently identified as the polymer $[\{\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\mu\text{-dpmm})\}]_n$ (**5**), is insoluble in all common solvents. Compound **4** can be prepared in high yield by treating **1** with dpmm in a 1:2 mol ratio.

Scheme 2. Reactivity of complex **1** with dpmm

The structure shown in Scheme 2 for complex **4** is substantiated by its analytical and spectroscopic data. In particular, its $^31\text{P}\{^1\text{H}\}$ -NMR spectrum, which consists of two multiplets at $\delta = 25.7$ and -24.9 (AA'XX' spin system), indicates that the two dpmm ligands are symmetry-related and that they are coordinated in a monodentate mode. The $\nu(\text{CO})$ region of its IR spectrum is comparable to those of compounds **3a**, **3b**, and **3c** (Table 1), indicating a similar arrangement of the carbonyl ligands (C_{2v} symmetry). Analogous spectral data have previously been reported for the related diruthenium(I) complexes $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_4(\eta^1\text{-dpmm})_2]$ ^[17] and $[\text{Ru}_2(\mu\text{-MeCO}_2)_2(\text{CO})_4(\eta^1\text{-dpmm})_2]$ ^[20], which contain *N*- and *O*-donor bridging ligands, respectively.

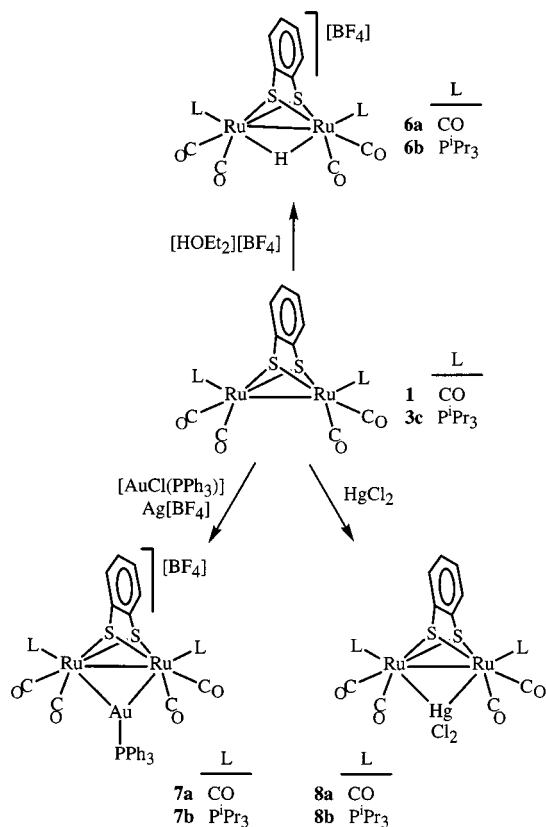
Due to its insolubility, compound **5** could only be characterized by microanalysis and IR spectroscopy. Nevertheless, we think that its structure is likely to be that depicted in Scheme 2, because the available data indicate that there is only one dpmm ligand per $\{\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4\}$ unit (CHN microanalysis) and that the local C_{2v} symmetry of the $\{\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4\}$ unit is maintained in the polymer since three $\nu(\text{CO})$ absorptions are observed in the IR spectrum (Table 1). It has been reported that the compounds $[\{\text{Ru}_2(\mu\text{-dan})(\text{CO})_4(\mu\text{-dpmm})\}]_n$ ^[17] and $[\{\text{Ru}_2(\mu\text{-MeCO}_2)_2(\text{CO})_4(\mu\text{-dpmm})\}]_n$ ^[20] also have a polymeric nature, in which the dpmm ligands linking the corresponding dimetallic units. However, the iodide-bridged compound $[\text{Ru}_2(\mu\text{-I})_2(\text{CO})_4(\mu\text{-dpmm})]$ is not polymeric and the dpmm ligand spans the same metal atoms as the iodide bridges^[21].

Reactions of Compounds **1** and **3c** with Electrophilic Reagents

The availability of both the hexacarbonyl compound **1** and the phosphane-substituted tetracarbonyl derivative **3c** allowed us to carry out a comparative study of their reactions with electrophilic reagents. Among the phosphane-substituted tetracarbonyl derivatives prepared from complex **1**, we decided to use **3c** for the reactivity studies because it contains the most basic phosphane ligand. Such a reactivity study would help us to determine whether or not the nucleophilic character of the dithiolate-bridged ruthenium(I) dimers is affected by the nature of the axial ligands. Furthermore, such a study, coupled to previous ones carried out with related complexes having *N*-donor bridging ligands^[17,22,23], would also shed light on the effect that the nature of the bridging ligand has on the nucleophilic character of this class of ligand-bridged ruthenium(I) dimers.

Both compounds, **1** and **3c**, could be protonated with an excess of $[\text{HOEt}_2][\text{BF}_4]$ in dichloromethane solvent to give the cationic derivatives $[\text{Ru}_2(\mu\text{-H})(\mu\text{-bdt})(\text{CO})_{6-n}(\text{P}i\text{Pr}_3)_n][\text{BF}_4]$ (**6a**: $n = 0$; **6b**: $n = 2$). Compound **6a** was unstable in solution and it undergoes spontaneous deprotonation in the absence of an excess of acid, even in solvents of low basicity such as dichloromethane or chloroform, to reform the neutral precursor **1**^[11]. However, the substituted derivative **6b**

is stable as far as deprotonation in solution is concerned. Curiously, it has been reported that the behavior of $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_6]$ ^[17] and $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_4(\text{P}i\text{Pr}_3)_2]$ ^[22] in protonation reactions is comparable to that observed for complexes **1** and **3c**.



Scheme 3. Reactions of compounds **1** and **3c** with electrophilic reagents

Compounds **1** and **3c** reacted with $[\text{AuCl}(\text{PPh}_3)]$ in the presence of $\text{Ag}[\text{BF}_4]$ to give AgCl and the cationic trinuclear derivatives $[\text{Ru}_2\text{Au}(\mu\text{-bdt})(\text{CO})_{6-n}(\text{P}i\text{Pr}_3)_n(\text{PPh}_3)][\text{BF}_4]$ (**7a**: $n = 0$; **7b**: $n = 2$). In related reactions, treatment of **1** and **3c** with mercury(II) chloride resulted in the formation of the corresponding adducts $[\text{Ru}_2\text{HgCl}_2(\mu\text{-bdt})(\text{CO})_{6-n}(\text{P}i\text{Pr}_3)_n]$ (**8a**: $n = 0$; **8b**: $n = 2$). Their IR spectra display the $\nu(\text{CO})$ absorptions shifted to higher wavenumbers than those of the corresponding starting materials (Table 1), confirming a decrease of electron density at the ruthenium atoms. The $^3\text{P}\{^1\text{H}\}$ -NMR spectra of the tetracarbonyl derivatives **7b** and **8b** indicate that both compounds have equivalent $\text{P}i\text{Pr}_3$ ligands since that of **7b** consists of an AX_2 spin system and that of **8b** is just a singlet, supporting the structures depicted in Scheme 3. It has been reported that the diamido-bridged compound $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_6]$ is not basic enough to react with the metallic electrophiles $[\text{Au}(\text{PPh}_3)]^+$ and HgCl_2 ^[17]; however, they do react with the disubstituted derivative $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_4(\text{P}i\text{Pr}_3)_2]$ to give the corresponding adducts^{[22][23]}. The related compound $[\text{Ru}_2(\mu\text{-dab})(\text{CO})_4(\text{PPh}_3)_2]$ also reacts with electrophilic metallic fragments to give stable adducts^[24].

All these data indicate that, in ligand-bridged diruthenium(I) carbonyl complexes, the basicity of the metal atoms is greatly affected by the nature of both the terminal and the bridging ligands. It was known that compounds having terminal phosphane ligands are more basic than their unsubstituted carbonyl precursors^{[22][23]}, but the results commented above experimentally demonstrate that complexes containing thiolate bridging ligands are more basic than their amido-bridged relatives. These results have also been confirmed by simple theoretical calculations at the extended Hückel level, which have shown that (a) the HOMOs of this kind of binuclear ligand-bridged ruthenium(I) complexes are of bonding character between the metal atoms, (b) that their composition is based mainly of orbitals belonging to the metal atoms^{[11][25]} and (c) that the positive charges beared by the metal atoms in $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_6]$ and $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_6]$ are higher than those beared by the substituted derivatives $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_4(\text{PH}_3)_2]$ and $[\text{Ru}_2(\mu\text{-bdt})(\text{CO})_4(\text{PH}_3)_2]$. These charges are expected to be inversely related to the basicity of the metal atoms in the complexes (the higher the charge, the less basic the metal atom), thus supporting the experimental reactivity results.

Experimental Section

General: Solvents were dried with sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons), molecular sieves (2-methoxyethanol) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. – Unless otherwise stated, the reactions were carried out under nitrogen at room temperature by Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). – The compounds **6a**^[11] and $[\text{AuCl}(\text{PPh}_3)]$ ^[26] were prepared as described in the literature, $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ was purchased from Pressure Chemicals, all other reagents were purchased from Aldrich. – IR: Perkin–Elmer FT 1720-X. – NMR: Bruker AC-200 and AC-300, 23°C, SiMe_4 (internal, for ^1H) or 85% H_3PO_4 (external, for ^{31}P) as standards ($\delta = 0$ ppm). – Microanalyses were obtained from the University of Oviedo Analytical Service.

One-Pot Synthesis of 1 from $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$: Carbon monoxide was bubbled through a solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (500 mg, 2.054 mmol) in 2-methoxyethanol (30 mL) at reflux temperature until the color changed to pale yellow (ca. 3 h). The addition of H_2bdt (130 μL , 1.130 mmol) was followed by addition of granular zinc (ca. 1 g). Maintaining the bubbling of carbon monoxide, the mixture was stirred at reflux temperature for 2 h to give an orange precipitate. After cooling to room temperature, the mixture was poured into a beaker containing water (500 mL). The tan precipitate was filtered through a celite pad. The solid was washed with water (3×5 mL), dried by passing air through the filter and extracted from the filter with dichloromethane. The extracts were concentrated to ca. 2 mL and the concentrate introduced into a chromatography column (2.5 $\times$ 10 cm) packed with neutral alumina (activity I) in hexane. After the column was washed with hexane, dichloromethane eluted a yellow band which afforded compound **1** as a yellow solid. – Yield: 270 mg (55%). – Its analytical and spectroscopic data matched those reported in the literature^[11].

Preparation of 2a, 2b, 2c, 3a, 3b, and 3c by Reaction of Compound 1 with Monodentate Phosphane Ligands: The appropriate amount

of the corresponding phosphane ligand was added to a solution of compound **1** in THF (10 mL). After being stirred at the appropriate temperature, the solvent was removed under reduced pressure and the residue was washed with hexane (2 × 2 mL) and dried under vacuum to give the product as a yellow solid.

2a: Reagents: 42 mg (0.082 mmol) of **1** and 22 mg (0.083 mmol) of PPh₃. – Reaction time: 3 h at room temperature. – Yield: 50 mg (81%). – C₂₉H₁₉O₅PRu₂S₂: calcd: C 46.77, H 2.57; found: C 46.54, H 2.55. – ¹H NMR (CDCl₃): δ = 7.44–7.22 (m, 15 H), 6.61 (m, 2 H), 6.24 (m, 2 H).

2b: Reagents: 80 mg (0.156 mmol) of **1**, 44 mg (0.156 mmol) of PCy₃. – Reaction time: 3 h at room temperature. – Yield: 80 mg (67%). – C₂₉H₃₇O₅PRu₂S₂: calcd: C 44.66, H 4.89; found: C 44.86, H 5.01. – ¹H NMR (CDCl₃): δ = 7.13 (m, 2 H), 6.60 (m, 2 H), 2.30–1.10 (m, 33 H).

2c: Reagents: 50 mg (0.098 mmol) of **1**, 18.4 μL (0.098 mmol) of P*i*Pr₃. – Reaction time: 10 min at room temperature. – Yield: 55 mg (78%). – C₂₀H₂₅O₅PRu₂S₂: calcd: C 37.38, H 3.92; found: C 37.02, H 3.94. – ¹H NMR (CDCl₃): δ = 7.11 (m, 2 H), 6.57 (m, 2 H), 2.10 (m, 3 H), 1.22 (m, 18 H).

3a: Reagents: 30 mg (0.059 mmol) of **1**, 33 mg (0.124 mmol) of PPh₃. – Reaction time: 20 min at reflux temperature. – Yield: 40 mg (70%). – C₄₆H₃₄O₄P₂Ru₂S₂: calcd: C 56.44, H 3.75; found: C 56.41, H 3.75. – ¹H NMR (CDCl₃): δ = 7.42–7.29 (m, 30 H), 6.06 (m, 2 H), 5.85 (m, 2 H).

3b: Reagents: 30 mg (0.059 mmol) of **1**, 33 mg (0.117 mmol) of PCy₃. – Reaction time: 40 min at reflux temperature. – Yield: 45 mg (78%). – C₄₆H₇₀O₄P₂Ru₂S₂: calcd: C 56.32, H 7.19; found: C 56.10, H 7.15. – ¹H NMR (CDCl₃): δ = 7.06 (m, 2 H), 6.54 (m, 2 H), 1.52–1.17 (m, 66 H).

3c: Reagents: 50 mg (0.098 mmol) of **1**, 46 μL (0.245 mmol) of P*i*Pr₃. – Reaction time: 25 min at reflux temperature. – Yield: 60 mg (79%). – C₂₈H₄₆O₄P₂Ru₂S₂: calcd: C 43.40, H 5.98; found: C 42.98, H 5.71. – ¹H NMR (CDCl₃): δ = 7.02 (m, 2 H), 6.47 (m, 2 H), 2.07 (m, 6 H), 1.22 (m, 36 H).

One-pot Synthesis of 3a, 3b, and 3c from RuCl₃ · *n* H₂O: Carbon monoxide was bubbled through a solution of RuCl₃ · *n* H₂O (500 mg, 2.054 mmol) in 2-methoxyethanol (30 mL) at reflux temperature until the color changed to pale yellow (ca. 3 h). The addition of H₂bdt (130 μL, 1.130 mmol) was followed by addition of granular zinc (ca. 1 g). Maintaining the bubbling of carbon monoxide, the mixture was stirred at reflux temperature for 15 min to give an orange precipitate. After adding the appropriate amount of the corresponding phosphane ligand (2.060 mmol), the mixture was cooled to room temperature under nitrogen and was stirred for 3 h. The suspension was filtered through a celite pad. The liquid phase was discarded off and the solid was extracted from the filter with dichloromethane. The extract was evaporated to dryness and the residue was washed with diethyl ether (2 × 3 mL) to give the corresponding product as a yellow solid. – Yields: 48% (**3a**), 43% (**3b**), and 73% (**3c**).

Preparation of 4: Solid dppm (75.3 mg, 0.196 mmol) was added to a solution of complex **1** (50 mg, 0.098 mmol) in THF (25 mL). The solution was stirred for 5.5 h and the solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 × 2 mL) and dried under vacuum to give complex **4** as a yellow solid. – Yield 90 mg (75%). – C₆₀H₄₈O₄P₄Ru₂S₂: calcd: C 58.74, H 4.05; found: C 58.92, H 3.95. – ¹H NMR (CDCl₃): δ = 7.1–7.3 (m, 40 H), 6.16 (m, 4 H) 2.96 (m, 4 H).

Preparation of 5: Solid dppm (37.6 mg, 0.098 mmol) was added to a solution of complex **1** (50 mg, 0.098 mmol) in THF (25 mL).

After stirring for 30 min, the IR spectrum showed a ca. 50% mixture of complexes **1** and **4**. After 4 h, a yellow solid began to precipitate. The mixture was stirred for 3 days, when the precipitate was copious and the liquid phase was nearly colorless. The liquid was decanted off and the solid was washed with THF (2 × 5 mL) and dried under vacuum. – Yield 90 mg (75%). – C₃₅H₂₆O₄P₂Ru₂S₂: calcd: C 50.12, H 3.12; found: C 49.38, H 3.02.

Preparation of 6b: An excess of [HOEt₂][BF₄] (4 drops from a pasteur pipette) was added to a solution of complex **1** (100 mg, 0.129 mmol) in dichloromethane (10 mL). The color of the solution changed from yellow to very pale yellow. The solvent was removed under reduced pressure and the oily residue was washed with diethyl ether (3 × 2 mL) to give complex **6b** as a white powder. – Yield 89 mg (80%). – C₂₈H₄₇BF₄O₄P₂Ru₂S₂: calcd: C 38.98, H 5.49; found: C 38.29, H 5.78. – ¹H NMR (CD₂Cl₂): δ = 7.24 (m, 2 H), 6.83 (m, 2 H), 2.20 (m, 6 H), 1.3 (m, 36 H), –16.16 (t, *J*_{H-P} = 29.5 Hz, 1 H).

Preparation of 7a and 7b: Solid Ag[BF₄] was added to a THF solution (15 mL) containing [AuCl(PPh₃)] and the appropriate ruthenium starting complex. A white precipitate of AgCl was immediately formed. The mixture was stirred for 30 min and the solvent was removed under reduced pressure. The residue was extracted with dichloromethane (3 × 5 mL) and the filtered solution was evaporated to dryness. The yellow solid was washed with diethyl ether (2 × 3 mL) and dried under vacuum.

7a: Reagents: 20 mg (0.039 mmol) of **1**, 19.3 mg (0.039 mmol) of [AuCl(PPh₃)], 7.6 mg (0.039 mmol) of Ag[BF₄]. – Yield: 29 mg (73%). – C₃₀H₁₉AuBF₄O₆Ru₂S₂: calcd: C 35.14, H 1.87; found: C 34.89, H 1.98. – ¹H NMR (CDCl₃): δ = 7.6–7.3. (m, 17 H), 6.88 (m, 2 H).

7b: Reagents: 50 mg (0.064 mmol) of **3c**, 31.7 mg (0.064 mmol) of [AuCl(PPh₃)], 13 mg (0.064 mmol) of Ag[BF₄]. – Yield: 60 mg (72%). – C₄₆H₆₁AuBF₄O₄P₂Ru₂S₂: calcd: C 42.83, H 4.77; found: C 42.91, H 4.83. – ¹H NMR (CDCl₃): δ = 7.57 (m, 15 H), 7.15 (m, 2 H), 6.78 (m, 2 H), 2.23 (m, 6 H), 1.72 (m, 36 H).

Preparation of 8a and 8b: Solid HgCl₂ was added to a solution of the appropriate ruthenium starting complex in THF (15 mL). The solution was stirred for 30 min to give a yellow solid (**8a**) or a yellow solution (**8b**). The solvent was removed under reduced pressure and the solid yellow residue was washed with diethyl ether (2 × 3 mL) and dried under vacuum.

8a: Reagents: 30 mg (0.059 mmol) of **1**, 16 mg (0.059 mmol) of HgCl₂. – Yield: 30 mg (65%). – C₁₂H₄Cl₂HgO₆Ru₂S₂: calcd: C 18.43, H 0.52; found: C 18.41, H 0.75. – ¹H NMR ([D₆]acetone): δ = 7.44 (m, 2 H), 6.92 (m, 2 H).

8b: Reagents: 50 mg (0.064 mmol) of **3c**, 17.5 mg (0.064 mmol) of HgCl₂. – Yield: 40 mg (60%). – C₂₈H₄₆Cl₂HgO₄P₂Ru₂S₂: calcd: C 32.14, H 4.43; found: C 31.83, H 4.36. – ¹H NMR (CDCl₃): δ = 7.19 (m, 2 H), 6.77 (m, 2 H), 2.21 (m, 6 H), 1.3 (m, 36 H).

Crystal Structure Determination of 3c: Crystal data and details of the structure determination are listed in Table 3. The unit cell dimensions were determined from the angular settings of 25 reflections with 15° < Θ < 20°. The orthorhombic space group *P*₂₁*nb* was determined from systematic absences and confirmed by the structure determination. The intensity was checked throughout data collection by monitoring three standard reflections every 60 min. Final drift correction factors were between 1.00 and 1.01. Profile analysis^[27] was performed on all reflections. A semiempirical absorption correction was applied, using ψ scans^[28] (correction factors were in the range 0.973 to 1.000). No doubly measured

reflections were obtained. Lorentz and polarization corrections were applied and data were reduced to $|F_o|^2$ values.

Table 3. Crystallographic and refinement data for complex **3c**

formula	C ₂₈ H ₄₆ O ₄ P ₂ Ru ₂ S ₂
fw	774.85
cryst syst	orthorhombic
space group	<i>P</i> 2 ₁ <i>nb</i>
<i>a</i> , <i>b</i> , <i>c</i> [Å]	11.503(1), 26.781(3), 11.023(2)
<i>V</i> [Å ³]	3395.9(9)
<i>Z</i>	4
<i>F</i> (000)	1584
<i>D</i> _{calcd} [g/cm ³]	1.516
absorption correction	ψ-scans
μ [mm ^{−1}]	1.136
cryst size [mm]	0.33 × 0.33 × 0.33
radiation (λ [Å])	Mo- <i>K</i> _α (0.71073)
diffractometer	Enraf-Nonius CAD4
monochromator	graphite
temp [K]	293 (2)
scan method	ω–2θ
min/max <i>h</i> , <i>k</i> , <i>l</i>	0 /13, 0/31, 0/13
θ range [°]	1.52 to 24.97
data set	3137
unique data	3137
data with <i>I</i> > 2σ(<i>I</i>)	2633
restraints, parameters	1, 383
<i>R</i> (<i>F</i>) _{<i>I</i> > 2σ(<i>I</i>)} ^[a]	0.0281
<i>R</i> _w (<i>F</i> ²) _{all data} ^[b]	0.0733
GOF ^[c]	1.027
Δ/σ	0.001
max, min Δρ [e/Å ³]	0.339, −0.409

^[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. — ^[b] $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, period — ^[c] Goodness of fit (GOF) = $[\sum w(F_o^2 - F_c^2)^2 / (N - P)]^{1/2}$.

The structure was solved by Patterson interpretation using the program DIRDIF92^[29]. An isotropic least-squares refinement, using a local version of SHELX^[30], was followed by an empirical absorption correction^[31] (maximum and minimum correction factors 1.547 and 0.698, respectively). Full-matrix anisotropic least-squares refinement over *F*², using the program SHELXL92^[32], followed by a difference Fourier synthesis allowed the location of all the hydrogen atoms. Positional parameters and anisotropic thermal parameters of the non-hydrogen atoms were refined. All hydrogen atoms were refined isotropically, constraining the bond angles but with free distances to their parent atoms. The thermal parameter used for the aliphatic hydrogen atoms was different from that used for the aromatic hydrogen atoms. The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0462 \cdot P)^2]$, with $\sigma(F_o)$ from counting statistics and $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors were taken from the literature^[33]. The plot in Figure 1 was made with the EUCLID package^[34]. Geometrical calculations were made with PARST^[35]. All computations were performed on an Alpha AXP3000 workstation.

Crystallographic data (excluding structure factors) for compound **3c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109933. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (1223) 336033, E-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk].

EHMO Calculations: Theoretical MO calculations were carried out at the extended Hückel level^[36], using the CACAO program^[37]. The geometrical parameters used were based on X-ray diffraction data, averaging the appropriate distances and angles in order to

obtain ideal C_{2v} symmetry. The orbital parameters used in the calculations were those used in previous works^[11].

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