Facile Syntheses, Isomeric Structures, and Chemical Reactivity of Diruthenium(I) Complexes $[Ru_2(CO)_4(MeCN)_4L_2]X_2$ (L = MeCN, PPh_3, PPh_2(allyl), PMe_3; $X^- = PF_6^-$, BF_4^-). A Convenient Route to 1,2-Diamides and 1,2-Dithiolates

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Alkylating agents such as $Et_3O^+X^-$ ($X^- = PF_6^-$ or BF_4^-) readily remove the bridging acetate groups of $[Ru_2(CO)_4(O_2CMe)_2L_2]$ at ambient temperature to give the versatile complexes $[Ru_2(CO)_4(NCMe)_4L_2]X_2$ (L = MeCN (**1**), PPh_3 (**2**), PPh_2(allyl) (**3**), and PMe_3 (**4**)). The crystal structures of **3** and **4** were determined by X-ray crystallography: $[\mathbf{3}][BF_4]_2$, $a = 20.292(6)$, $b = 17.223(7)$, $c = 15.186(3)$, $\beta = 113.324(18)°$, $V = 4873(3)$ Å^3, monoclinic $C2/c$, $Z = 4$, refined to $R = 0.045$, $R_w = 0.048$, and GOF = 2.27. $[\mathbf{4}][BF_4]_2$, $a = 12.570(4)$, $b = 14.251(5)$, $c = 18.773(6)$ Å, $\beta = 104.96(3)°$, $V = 3251(9)$ Å^3, monoclinic $P2_1/n$, $Z = 4$, refined to $R = 0.044$, $R_w = 0.044$, and GOF = 1.53. Although **3** adopts a *trans*-staggered structure, **4** is in a *cis*-staggered geometry. The high reactivity of **1**–**4** is demonstrated via the cation–anion annihilation between $\mathbf{2}^{2+}$ and the doubly deprotonated anion, $(E-E)^{2-}$, to give $[Ru_2(CO)_4\{\mu\text{-}\eta^2,\eta^2\text{-}(E\text{-}E)\}(PPh_3)_2]$ ($(E-E)^{2-}$ = 1,2-$(NH)_2C_6H_4^{2-}$ (**7**); 2,3-$(NH)_2C_{10}H_6^{2-}$ (**8**); 1,2-$(NH)_2$-4,5-$Cl_2C_6H_2^{2-}$ (**9**); 1,2-$(NH)_2$-4,5-$Me_2C_6H_2$ (**10**); 9,10-$(NH)_2C_{14}H_8$ (**11**); and 1,2-$S_2C_6H_4^{2-}$ (**12**)). The structures of **7**–**12** were also confirmed by an X-ray single-crystal structure of **12**: $a = 11.155(1)$, $b = 21.302(2)$, $c = 10.183(2)$ Å, $\alpha = 93.65(1)$, $\beta = 113.43(1)$, $\gamma = 101.19(1)°$, $V = 2151.2(6)$ Å^3, triclinic $P\bar{1}$, $Z = 2$, refined to $R = 0.038$, $R_w = 0.046$, and GOF = 2.81. The Ru–Ru distances are 2.8647(11) Å in **3**, 2.861(1) Å in **4**, and 2.6767(5) Å in **12**.

Introduction

Multinuclear metal carbonyl complexes of doubly anionic difunctional ligands, $(E-E)^{2-}$, prepared from heterocylic compounds such as 1,2-diaminobenzene,[1] 1,2-bis(phenylphosphino)benzene,[2] 1,8-diaminonaphthalene,[3] or catechol[4] have recently been active areas of research, probably due to the related rich coordination chemistry, especially that involving *controlled* aggregation and/or fragmentation pathways[5] of the metal–metal bonds. Recognition of the fact that dinuclear compounds can be either fragmented into mononuclear products or aggregated into tri- or higher-nuclear cluster compounds, mediated by the ligands, prompted us to find a facile approach, as shown below, to ligated dinuclear compounds. It involves acetate removal from $[Ru_2(CO)_4(MeCO_2)_2L_2]$ to form $[Ru_2(CO)_4(MeCN)_4L_2]^{2+}$ and then cation–anion annihilation with $(E-E)^{2-}$ to readily give $[Ru_2(CO)_4\{\mu\text{-}\eta^2,\eta^2\text{-}(E-E)\}L_2]$ (Scheme 1).

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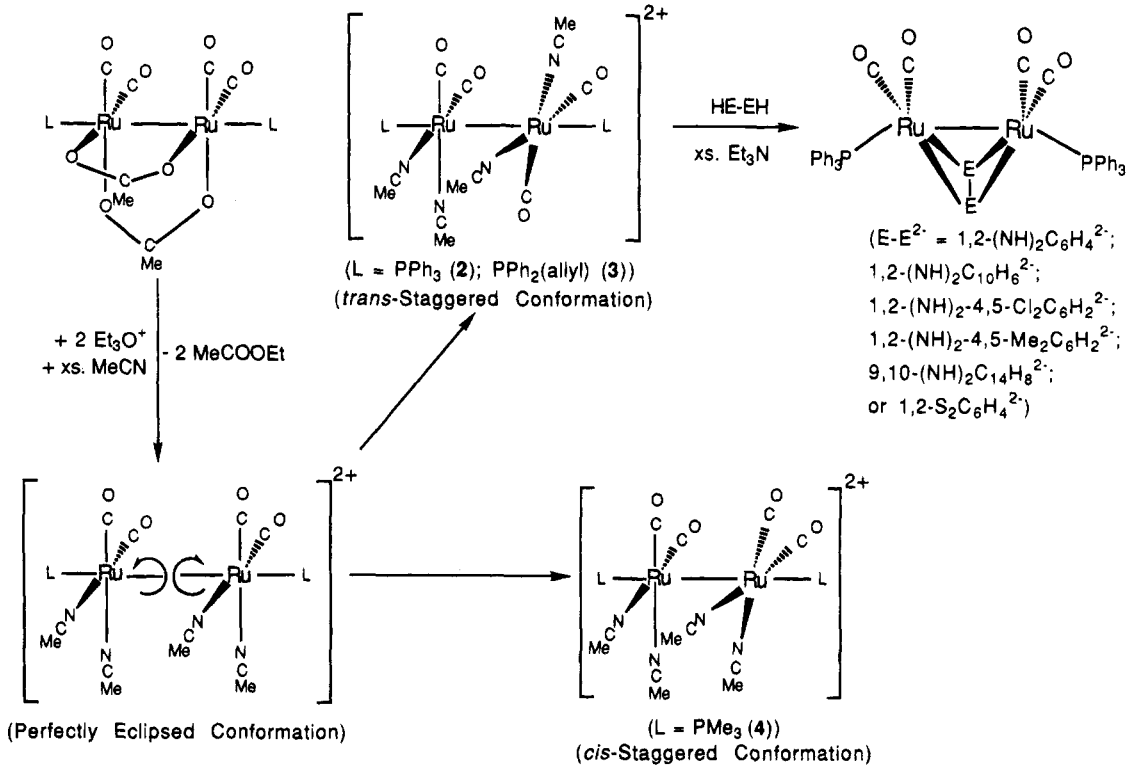
Scheme 1



Results and Discussion

Partial or total removal of the acetate groups in dinuclear complexes such as $[M_2(O_2CMe)_4]$ (M = Mo or Rh) by treatment of the complexes with strong acids or alkylating reagents is well-known in the literature.[6] We now report that the acetate-removal approach using alkylating reagents works equally well in metal carbonyl complexes of acetates such as $[Ru_2(CO)_4(MeCO_2)_2L_2]$ in the presence of a weakly coordinating solvent such as MeCN, giving $[Ru_2(CO)_4(MeCN)_4L_2]X_2$ (L = MeCN (**1**), PPh_3 (**2**), PPh_2(allyl) (**3**), and PMe_3 (**4**)) nearly quantitatively.

Following addition of an alkylating reagent to a solution of $[Ru_2(CO)_4(MeCO_2)_2L_2]$ in CH_2Cl_2 and MeCN, three new carbonyl stretching bands and one shoulder having strong intensities (for **1**–**4**) and two other new bands with medium intensities at 1758 and 1728 cm^{-1} (probably due to ethyl acetate and related derivatives) were soon observed in the solution IR spectrum. The reaction is usually complete within 30 min. Longer or shorter time needed for a complete conversion appears dependent on the specific L used. The two acetate groups of $[Ru_2(CO)_4(MeCO_2)_2L_2]$ were first probably converted into ethyl acetate and then replaced quickly by the MeCN to give **1**–**4**. Compounds $[\mathbf{1}][PF_6]_2$ and $[\mathbf{2}][PF_6]_2$ were reported in 1993 but prepared by a somewhat tedious procedure from $[Ru_2(CO)_6Cl_2]$.[7]

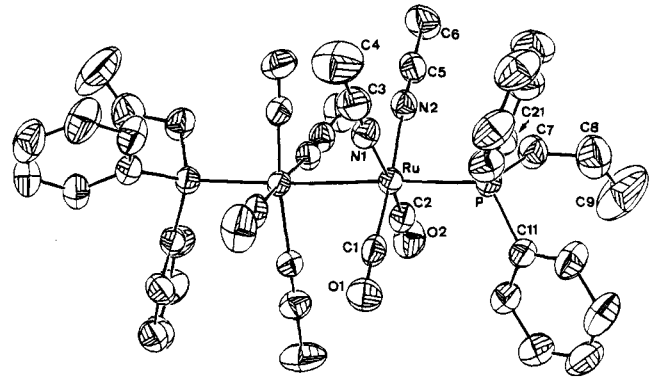


Figure 1. ORTEP representation with 50% probability ellipsoids of $[Ru_2(CO)_4(MeCN)_4\{PPh_2(allyl)\}_2]^{2+}$ ($\mathbf{3}^{2+}$).

Intrigued by the unexpected steric effect of propeller configurations of a PPh_3 ligand to induce isomerism,[8] we determined the structures of $[\mathbf{3}][BF_4]_2$ (Figure 1) and $[\mathbf{4}][BF_4]_2$ (Figure 3) even though that of $[\mathbf{2}][PF_6]_2$ was reported previously.[7] Selected bond distances and angles are listed in Table 1. From Figures 1 and 3, it is quite obvious that the two phosphine ligands occupy positions *trans* to the Ru–Ru bond in $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$ with the torsional angles P′–Ru′–Ru–P = 143.6(1)° in $\mathbf{3}^{2+}$ and P(1)–Ru(1)–Ru(2)–P(2) = 178.7(1)° in $\mathbf{4}^{2+}$, although like $\mathbf{2}^{2+}$, only $\mathbf{3}^{2+}$ contains a crystallographically imposed C_2 axis. To our surprise, and in contrast to cations $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$, which are similar to each other in having a *trans*-staggered conformation (Figure 2), cation $\mathbf{4}^{2+}$ has a *cis*-staggered conformation (Figure 4), similar to the related triazolylborate complexes $[Ru\{HB(pz)_3\}_2(CO)_4]$ (**5**) and $[Ru\{HB(tz)_3\}_2(CO)_4]$ (**6**) (pz = 1-pyrazolyl; tz = 1,2,4-triazolyl).[9] The conformations observed in **3** and **4** can be achieved by rotating the two *cis*-$Ru(CO)_2$

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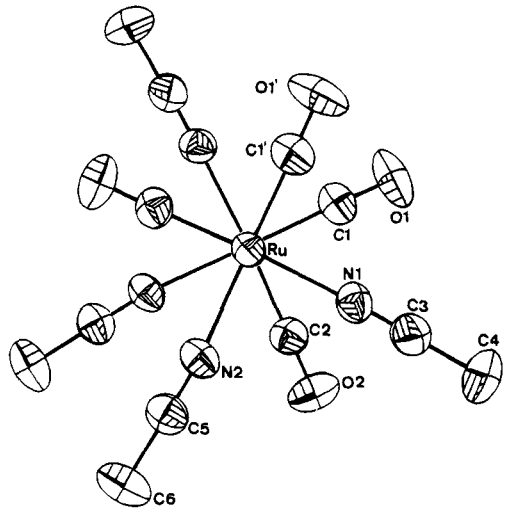

Figure 2. Projection of cation 3^{2+} down the Ru–Ru bond (two PPh_2(allyl) groups have been omitted for clarity).

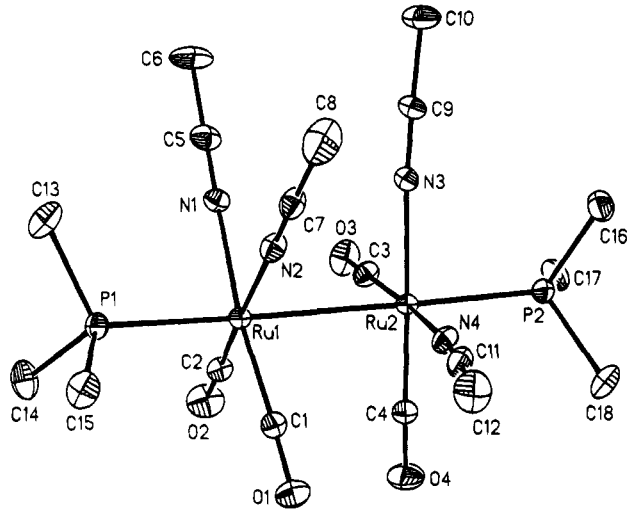

Figure 3. ORTEP representation with 50% probability ellipsoids of $[Ru_2(CO)_4(MeCN)_4(PMe_3)_2]^{2+}$ (4^{2+}).

groups of a perfectly eclipsed conformation away from each other to form a twist angle of 130.9° in 3^{2+} and 43.8° in 4^{2+} (Scheme 1). The Ru–Ru distance of 2.861(1) Å in **4** is the shortest one among all the reported values (2.8647(11) Å in **3**, 2.8731(8) Å in **2**,[7] 2.8688(7) Å in **6**, and 2.882(1) Å in **5**[9]). If the significantly shorter Ru–Ru bond length in **3** relative to that in **2**[7] is attributed to the smaller PPh_2(allyl) (Tolman cone angle 140°)[10] relative to PPh_3 (Tolman cone angle 145°),[11] the nearly identical Ru–Ru bond lengths in **3** and **4** should be explained by considering both the steric (Tolman cone angle 118°)[11] and electronic[12] effects of PMe_3. However, it is not presently known for sure whether the steric or the electronic effect is more important, determining the preferred conformation of the phosphine ligands in **2**–**4**.

Reaction of **2** with various heterocyclic compounds, HE–EH, in the presence of excess Et_3N, afforded the yellow crystalline dinuclear products $[Ru_2(CO)_4(E–E)(PPh_3)_2]$ ((E–E)$^{2-}$ = 1,2-$(NH)_2C_6H_4^{2-}$ (**7**); 2,3-$(NH)_2C_{10}H_6^{2-}$ (**8**); 1,2-$(NH)_2$-4,5-$Cl_2C_6H_2^{2-}$ (**9**); 1,2-$(NH)_2$-4,5-$Me_2C_6H_2$ (**10**); 9,10-$(NH)_2C_{14}H_8$ (**11**), and 1,2-$S_2C_6H_4^{2-}$ (**12**)) in 85–95% yield. The synthesis of **7** was reported earlier, but with a lower yield, from carbonylation of $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)_3]$, from a reaction between this compound and $Cr(CO)_6$, or from that between $[Ru(CO)_3(PPh_3)_2]$ and 1,2-$(NH_2)_2C_6H_4$.[1] Since the spectral data of **8**–**12** are quite similar to those of **7**, the structures of **8**–**12** are believed to be, like that of **7**, to have an almost perpendicular (E–E) plane. Indeed, confirmation was also provided by an X-ray diffraction study of **12** (Figure 5), which revealed a longer Ru–Ru bond length (2.6767(5) Å in **12** versus 2.560(1) Å in **7**[1]).

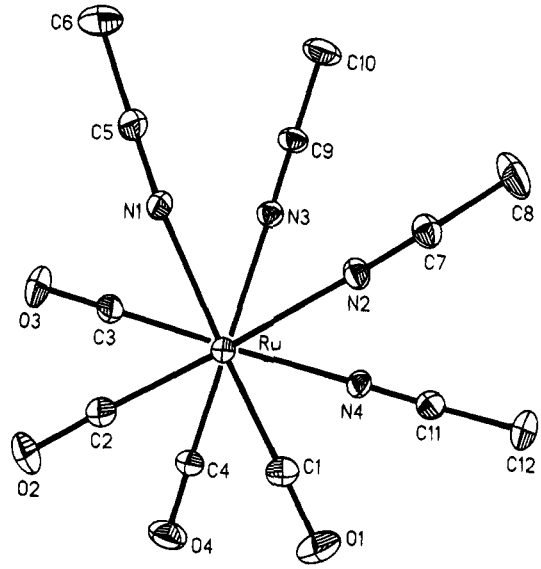

Figure 4. Projection of cation 4^{2+} down the Ru–Ru bond (two PMe_3 groups have been omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3, 4, and 12

Bond Lengths for 3					
Ru–Ru′	2.8647(11)	Ru–P	2.3843(18)	Ru–C(1)	1.855(8)
Ru–C(2)	1.848(8)	Ru–N(1)	2.102(6)	Ru–N(2)	2.100(5)
C(1)–O(1)	1.140(10)	C(2)–O(2)	1.142(9)		
Bond Angles for 3					
P–Ru–C(1)	93.60(20)	P–Ru–C(2)	95.66(21)		
P–Ru–N(1)	91.31(16)	P–Ru–N(2)	89.50(15)		
P–Ru–Ru′	176.45(5)				
Bond Lengths for 4					
Ru(1)–Ru(2)	2.861(1)	Ru(1)–P(1)	2.383(2)	Ru(1)–C(1)	1.855(7)
Ru(1)–C(2)	1.848(8)	Ru(1)–N(1)	2.105(6)	Ru(1)–N(2)	2.107(6)
C(1)–O(1)	1.148(10)	C(2)–O(2)	1.153(10)	Ru(2)–P(2)	2.381(2)
Ru(2)–C(3)	1.867(8)	Ru(2)–C(4)	1.854(8)	Ru(2)–N(3)	2.097(6)
Ru(2)–N(4)	2.104(7)	C(3)–O(3)	1.136(11)	C(4)–O(4)	1.146(10)
Bond Angles for 4					
P(1)–Ru(1)–C(1)	93.8(3)	P(1)–Ru(1)–C(2)	97.1(3)		
P(1)–Ru(1)–N(1)	91.5(2)	P(1)–Ru(1)–N(2)	86.5(2)		
P(2)–Ru(2)–C(3)	97.0(3)	P(2)–Ru(2)–C(4)	92.6(3)		
P(2)–Ru(2)–N(3)	89.4(2)	P(2)–Ru(2)–N(4)	89.2(2)		
P(1)–Ru(1)–Ru(2)	172.1(1)	P(2)–Ru(2)–Ru(1)	174.8(1)		
Bond Lengths for 12					
Ru(1)–Ru(2)	2.6767(5)	Ru(1)–S(1)	2.433(1)	Ru(1)–S(2)	2.415(1)
Ru(1)–P(1)	2.362(1)	Ru(1)–C(43)	1.869(5)	Ru(1)–C(44)	1.866(5)
Ru(2)–S(1)	2.415(1)	Ru(2)–S(2)	2.430(1)	Ru(2)–P(2)	2.365(1)
Ru(2)–C(45)	1.864(5)	Ru(2)–C(46)	1.827(5)	C(43)–O(1)	1.144(5)
C(44)–O(2)	1.148(5)	C(45)–O(3)	1.152(6)	C(46)–O(4)	1.162(7)
Bond Angles for 12					
Ru(1)–S(1)–Ru(2)	67.02(3)	Ru(1)–S(2)–Ru(2)	67.08(3)		
P(1)–Ru(1)–Ru(2)	151.70(3)	P(2)–Ru(2)–Ru(1)	151.51(3)		

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(10) Since the size of PPh_2Et is similar to that of PPh_2(allyl), the Tolman cone angle of 140° for PPh_2Et is used for that of PPh_2(allyl).[11]

(11) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(12) In the related $[Ru_2(CO)_4(MeCO_2)_2L_2]$ system, it was found that a better electron donor may lengthen the Ru–Ru bond.[13]

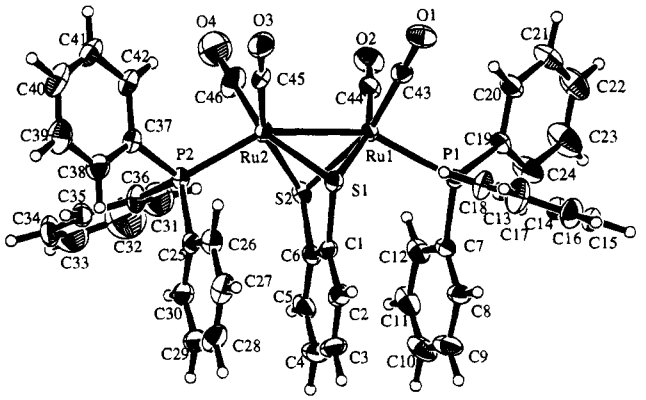

Figure 5. ORTEP representation with 50% probability ellipsoids of **12**.

Table 2. Fractional Atomic Coordinates and B_{eq} for 3

	x	*y*	*z*	B_{eq},[a] Å^2
Ru	0.00037(3)	0.28703(3)	0.15587(4)	2.99(3)
P	0.00851(9)	0.28435(11)	0.00353(12)	3.39(8)
C1	0.0340(4)	0.3882(4)	0.1817(5)	4.1(4)
O1	0.0558(4)	0.4500(3)	0.1964(4)	6.8(4)
C2	0.0916(4)	0.2488(4)	0.2242(5)	3.9(4)
O2	0.1481(3)	0.2255(4)	0.2664(4)	5.9(3)
N1	−0.1065(3)	0.3257(3)	0.0933(4)	3.8(3)
C3	−0.1648(5)	0.3433(4)	0.0572(6)	4.7(4)
C4	−0.2402(5)	0.3647(6)	0.0111(8)	7.9(6)
N2	−0.0392(3)	0.1728(3)	0.1332(4)	3.8(3)
C5	−0.0544(4)	0.1089(5)	0.1243(5)	4.2(4)
C6	−0.0716(5)	0.0264(5)	0.1149(6)	6.3(5)
C7	0.0341(4)	0.1877(4)	−0.0249(6)	4.9(4)
C8	0.0495(6)	0.1806(6)	−0.1092(7)	7.5(7)
C9	0.1167(8)	0.1730(8)	−0.1029(13)	13.7(14)
C11	0.0756(4)	0.3468(4)	−0.0120(5)	3.8(4)
C12	0.1403(4)	0.3594(5)	0.0625(6)	5.5(5)
C13	0.1946(5)	0.3984(6)	0.0482(7)	6.9(6)
C14	0.1842(6)	0.4253(6)	−0.0406(9)	6.9(6)
C15	0.1195(6)	0.4149(6)	−0.1153(7)	6.8(6)
C16	0.0644(4)	0.3755(5)	−0.1023(6)	5.4(4)
C21	−0.0756(4)	0.3102(4)	−0.0935(5)	3.8(4)
C22	−0.1218(4)	0.2539(5)	−0.1502(6)	5.5(5)
C23	−0.1882(5)	0.2760(6)	−0.2186(7)	6.8(5)
C24	−0.2086(4)	0.3518(7)	−0.2289(7)	6.6(5)
C25	−0.1643(5)	0.4081(5)	−0.1725(7)	5.7(5)
C26	−0.0973(4)	0.3876(5)	−0.1035(5)	4.7(4)
B	0.6466(10)	0.4791(10)	0.1675(13)	8.6(10)
F1	0.5942(6)	0.4420(5)	0.1208(9)	19.7(8)
F2	0.6871(6)	0.5007(10)	0.1283(9)	24.0(13)
F3	0.6306(9)	0.5444(8)	0.1885(16)	26.4(20)
F4	0.6822(8)	0.4540(13)	0.2422(10)	30.1(16)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}a^*c^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

If planes **1**−**3** are defined to include C(1)−C(6), C(7)−C(12), and C(25)−C(30) atoms, respectively, the angles formed by any two planes are 8.6° between planes **1** and **2**, 2.4° between planes **1** and **3**, and 6.3° between planes **2** and **3**. In other words, the three phenyl planes are almost parallel to each other. Apparently, the specific propeller configuration of PPh_2R (R = Ph or allyl) influences not only the structures of **2** and **3** but that of **12**. As with structure **7**,[1] structure **12** has the low Ru−S−Ru angles (67.02(3) and 67.08(3)°) and similar Ru−S distances (2.415(1), 2.415(1), 2.430(1), and 2.433(1) Å).

Conclusions

Our investigation into the controlled aggregation and/or fragmentation pathways of metal−metal bonds has resulted in the synthesis of a variety of 1,2-diamides and -dithiolates and several novel molecular structures.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for 4

	x	*y*	*z*	U_{eq}[a]
Ru(1)	1688(1)	1850(1)	153(1)	28(1)
Ru(2)	3392(1)	1910(1)	−605(1)	29(1)
P(1)	285(2)	2030(1)	788(1)	35(1)
P(2)	4802(2)	2111(2)	−1228(1)	38(1)
F(1)	972(10)	6236(13)	1708(11)	219(10)
F(2)	1885(14)	5339(17)	1226(12)	253(12)
F(3)	2719(15)	6362(22)	2008(13)	316(16)
F(4)	1881(30)	5340(18)	2344(18)	345(22)
F(5)	6124(11)	3674(12)	1890(10)	205(9)
F(6)	6626(11)	3955(16)	871(7)	213(10)
F(7)	7808(12)	3362(18)	1775(11)	262(13)
F(8)	7178(23)	4722(16)	1665(17)	315(19)
O(1)	3498(6)	2355(6)	1486(4)	72(3)
O(2)	2146(7)	−179(4)	538(5)	75(3)
O(3)	2543(6)	70(5)	−1305(4)	68(3)
O(4)	4921(6)	861(5)	629(4)	72(3)
N(1)	514(6)	1548(4)	−842(3)	37(2)
N(2)	1395(5)	3265(5)	−162(4)	39(2)
N(3)	2306(5)	2660(5)	−1448(4)	38(2)
N(4)	3830(5)	3210(5)	−79(4)	40(2)
B(1)	1930(11)	5844(11)	1819(9)	75(5)
B(2)	6937(11)	3836(12)	1572(8)	74(5)
C(1)	2817(7)	2163(6)	970(5)	43(3)
C(2)	1981(7)	597(6)	371(5)	42(3)
C(3)	2852(7)	768(6)	−1039(5)	45(3)
C(4)	4318(7)	1259(6)	165(5)	43(3)
C(5)	−130(8)	1453(6)	−1378(5)	52(3)
C(6)	−969(12)	1359(10)	−2069(7)	88(5)
C(7)	1215(7)	4019(6)	−351(5)	44(3)
C(8)	1010(9)	4976(7)	−612(9)	82(5)
C(9)	1776(7)	3061(6)	−1947(4)	45(3)
C(10)	1130(9)	3582(9)	−2565(6)	73(4)
C(11)	3988(6)	3894(6)	234(5)	44(3)
C(12)	4107(9)	4766(7)	647(6)	64(4)
C(13)	−1041(7)	2383(8)	212(7)	65(4)
C(14)	−31(9)	1017(7)	1274(6)	63(4)
C(15)	616(8)	2916(6)	1507(6)	55(3)
C(16)	4587(8)	3079(7)	−1879(5)	55(3)
C(17)	5062(9)	1117(7)	−1756(6)	60(4)
C(18)	6126(8)	2377(9)	−596(7)	75(4)

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

The techniques that we have developed provide convenient routes to the synthesis of these materials and may be potentially applicable to a wide variety of other systems. Synthesis and reactivity of other diruthenium(I) complexes analogous to **1**−**4** and pyrolysis experiments of **7**−**12** in the presence or absence or other metal carbonyl complexes are in progress.

Experimental Section

General Comments. All solvents were dried and purified by standard methods (ethers, paraffins, and arenes from potassium with benzophenone as indicator; halocarbons and acetonitrile from CaH_2 and alcohols from the corresponding alkoxide) and were freshly distilled under nitrogen immediately before use. All reactions and manipulations were carried out in standard Schlenk ware, connected to a switchable double method providing vacuum and nitrogen. Reagents were used as supplied by Aldrich. ^1H and ^{31}P NMR spectra were measured on on a Bruker AMC-400 or a Varian Unity Plus-400 (^1H, 400 MHz; ^{31}P, 162 MHz) NMR spectrometer. ^1H Chemical shifts (δ in ppm, *J* in Hz) are defined as positive downfield relative to internal $MeSi_4$ (TMS) or the deuterated solvent, while ^{31}P chemical shifts are defined as positive downfield relative to external 85% H_3PO_4. The IR spectra, calibrated with polystyrene, were recorded on a Hitachi Model 270-30 instrument. The following abbrevations were used: s, strong; m, medium; w, weak. Microanalyses were carried out

Table 4. Atomic Coordinates and B_{eq} for 12

atom	x	y	z	B_{eq},[a] Å^2
Ru(1)	0.41265(4)	0.19004(2)	0.53736(4)	2.619(8)
Ru(2)	0.60012(4)	0.30205(2)	0.63735(4)	2.923(9)
S(1)	0.3882(1)	0.28796(5)	0.4289(1)	3.01(3)
S(2)	0.6038(1)	0.21353(6)	0.4773(1)	3.41(3)
P(1)	0.2568(1)	0.10739(5)	0.3469(1)	2.73(3)
P(2)	0.7451(1)	0.39017(6)	0.6042(1)	2.98(3)
O(1)	0.2293(4)	0.2005(2)	0.6852(4)	5.6(1)
O(2)	0.5430(4)	0.1020(2)	0.7409(4)	5.8(1)
O(3)	0.4961(4)	0.3789(2)	0.8096(4)	6.1(1)
O(4)	0.8024(6)	0.2724(3)	0.9085(6)	9.1(1)
C(1)	0.4315(5)	0.2715(2)	0.2817(5)	3.3(1)
C(2)	0.3678(6)	0.2900(2)	0.1484(6)	4.6(1)
C(3)	0.4078(8)	0.2767(3)	0.0386(6)	6.0(2)
C(4)	0.5114(8)	0.2469(3)	0.0642(7)	6.2(2)
C(5)	0.5755(6)	0.2275(2)	0.1970(6)	4.8(1)
C(6)	0.5338(5)	0.2395(2)	0.3054(5)	3.5(1)
C(7)	0.3111(5)	0.0912(2)	0.2029(5)	3.3(1)
C(8)	0.2466(6)	0.1045(2)	0.0662(6)	4.3(1)
C(9)	0.2986(8)	0.0948(3)	−0.0366(7)	6.1(2)
C(10)	0.4140(8)	0.0728(3)	0.0002(8)	6.6(2)
C(11)	0.4788(7)	0.0599(3)	0.1372(8)	5.7(2)
C(12)	0.4299(6)	0.0697(2)	0.2399(6)	4.5(1)
C(13)	0.0872(4)	0.1195(2)	0.2485(5)	3.0(1)
C(14)	−0.0179(5)	0.0688(2)	0.1549(5)	4.0(1)
C(15)	−0.1441(5)	0.0793(3)	0.0782(6)	4.7(1)
C(16)	−0.1682(5)	0.1393(3)	0.0943(7)	5.6(2)
C(17)	−0.0668(6)	0.1890(3)	0.1873(7)	6.2(2)
C(18)	0.0610(5)	0.1793(2)	0.2636(6)	4.6(1)
C(19)	0.2200(5)	0.0282(2)	0.4003(5)	3.3(1)
C(20)	0.1909(6)	0.0247(3)	0.5205(6)	4.8(1)
C(21)	0.1586(7)	−0.0344(3)	0.5631(7)	6.3(2)
C(22)	0.1571(7)	−0.0904(3)	0.4898(9)	6.7(2)
C(23)	0.1847(8)	−0.0882(3)	0.3708(9)	8.2(2)
C(24)	0.2167(7)	−0.0292(3)	0.3258(7)	6.0(2)
C(25)	0.6762(5)	0.4144(2)	0.4267(5)	3.3(1)
C(26)	0.5666(5)	0.4425(2)	0.3899(6)	4.2(1)
C(27)	0.5075(6)	0.4590(3)	0.2543(7)	5.5(2)
C(28)	0.5531(7)	0.4457(3)	0.1525(7)	6.2(2)
C(29)	0.6568(7)	0.4169(3)	0.1836(7)	5.8(2)
C(30)	0.7204(5)	0.4013(2)	0.3201(6)	4.3(1)
C(31)	0.9259(9)	0.3180(4)	0.6165(9)	8.9(2)
C(32)	1.048(1)	0.3063(5)	0.620(1)	13.6(3)
C(33)	1.1493(9)	0.3576(4)	0.6301(9)	9.0(2)
C(34)	1.1344(6)	0.4167(3)	0.6462(7)	5.9(2)
C(35)	1.0134(5)	0.4280(2)	0.6363(6)	4.1(1)
C(36)	0.9088(5)	0.3783(2)	0.6215(6)	4.0(1)
C(37)	0.7932(5)	0.4662(2)	0.7272(5)	3.6(1)
C(38)	0.8172(6)	0.5267(3)	0.6870(6)	5.0(1)
C(39)	0.8584(7)	0.5834(3)	0.7868(8)	6.7(2)
C(40)	0.8729(6)	0.5787(3)	0.9249(8)	6.3(2)
C(41)	0.8500(6)	0.5203(3)	0.9676(6)	5.4(2)
C(42)	0.8099(5)	0.4639(2)	0.8704(6)	4.3(1)
C(43)	0.2980(5)	0.1968(2)	0.6278(5)	3.5(1)
C(44)	0.4913(5)	0.1350(2)	0.6632(5)	3.7(1)
C(45)	0.5383(5)	0.3503(2)	0.7452(5)	3.8(1)
C(46)	0.7259(6)	0.2837(3)	0.8012(6)	6.0(2)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*c^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

Synthesis of $[Ru_2(CO)_4(MeCN)_4L_2]X_2$ (L = MeCN (1), PPh_3 (2), PPh_2(allyl) (3), and PMe_3 (4); $X^- = PF_6^-$, BF_4^-). The preparations of **1**–**4** are similar to each other. A typical procedure for **3** is described below. A mixture of $[Ru_2(CO)_4(MeCO_2)_2\{PPh_2(allyl)\}_2]$[14] (0.41 g, 0.46 mmol), MeCN (1 mL), and CH_2Cl_2 (25 mL) was added dropwise to $Et_3O^+BF_4^-$ (2 mL, 1.0 M solution in CH_2Cl_2). The solution was stirred for 30 min at ambient temperature (ca. 28 °C), and volatiles were removed under vacuum to give an oily solid. MeOH (ca. 5 mL) was then added, and the suspension was stirred for 10 min to destroy excess $Et_3O^+BF_4^-$. Filtration gave an yellow solid, which was then washed with Et_2O (2 mL) and dried under vacuum to give the pure product of $[3][BF_4]_2$ (0.63 g, 93%). Anal. Calcd for $C_{42}H_{42}B_2F_8N_4O_4P_2Ru_2$: C, 45.67; H, 3.83; N, 5.07. Found: C, 45.45; H, 3.80; N, 5.16. ^{1}H NMR (25 °C, CD_3CN, 400 MHz): δ 2.11 (s, 12 H), 3.45 (m, 4 H), 4.97 (m, 2 H), 5.06 (m, 2 H), 5.58 (m, 2 H), 7.56 (m, 2 H). $^{31}P\{^1H\}$ NMR (25 °C, CD_3CN, 162 MHz): δ 17.34. IR (CH_2Cl_2): ν_{CN}, 2296 w, 2260 w; ν_{CO}, 2048 s, 2024 s, 1990 s, 1980 sh cm^{-1}. For $[4][BF_4]_2$. Anal. Calcd for $C_{18}H_{30}B_2F_8N_4O_4P_2Ru_2$: C, 26.89; H, 3.76; N, 6.97. Found: C, 26.70; H, 3.81; N, 6.85. ^{1}H NMR (25 °C, CD_3CN, 400 MHz): δ 1.65 (t, $J_{P,H}$ = 4.8 Hz, 18 H), 1.96 (s, 12 H). $^{31}P\{^1H\}$ NMR (25 °C, CD_3CN, 162 MHz): δ −9.99. IR (CH_2Cl_2): ν_{CN}, 2296 w, 2252 w; ν_{CO}, 2044 s, 2016 s, 1974 s, 1954 sh cm^{-1}.

Synthesis of $[Ru_2(CO)_4](E-E)(PPh_3)_2]$ ($(E-E)^{2-}$ = 1,2-$(NH)_2C_6H_4^{2-}$ (7); 2,3-$(NH)_2C_{10}H_6^{2-}$ (8); 1,2-$(NH)_2$-4,5-Cl_2-$C_6H_2^{2-}$ (9); 1,2-$(NH)_2$-4,5-$Me_2C_6H_2$ (10); 9,10-$(NH)_2C_{14}H_8$ (11), and 1,2-$S_2C_6H_4^{2-}$ (12)). The preparations of **7**–**12** are similar to each other. A typical procedure for **10** is described below. In a 100-mL Schlenk flask was dissolved $[2][BF_4]_2$ (0.168 g, 0.143 mmol) in 15 mL of MeCN at room temperature. 4,5-Dimethyl-1,2-phenylenediamine (0.039 g, 0.29 mmol) and 0.2 mL of Et_3N were added to the Ru solution. The mixture was then heated at 82 °C for 1 h and cooled to room temperature. After the volatiles were pumped off, the residue was dissolved in 15 mL of CH_2Cl_2, filtered through a bed of Celite 2 cm deep, added to 10 mL of MeOH, and concentrated to 10 mL, producing yellow microcrystals. Filtration through a medium frit gave the product **10** (0.16 g, 85%). Anal. Calcd for $C_{48}H_{40}N_2O_4P_2Ru_2$: C, 59.26; H, 4.14; N, 2.88. Found: C, 58.55; H, 4.12; N, 2.82. ^{1}H NMR (25 °C, $CDCl_3$, 400 MHz): δ 1.37 (s, 6 H), 2.12 (s, 2 H), 4.64 (s, 2 H), 7.29 (m, 30 H). $^{31}P\{^1H\}$ (25 °C, $CDCl_3$, 162 MHz): δ 28.15. IR (CH_2Cl_2): ν_{CO}, 2000 s, 1966 m, 1926 s cm^{-1}. For **6**. Anal. Calcd for $C_{50}H_{36}N_2O_4P_2Ru_2$: C, 60.48; H, 3.65; N, 2.82. Found: C, 60.46; H, 3.63; N, 2.74. ^{1}H NMR (25 °C, acetone-d_6, 400 MHz): δ 4.16 (s, 2 H), 5.31 (s, 2 H), 6.44 (m, 2 H), 6.58 (m, 2 H), 7.27 (m, 30 H). $^{31}P\{^1H\}$ (25 °C, acetone-d_6, 162 MHz): δ 34.15. IR (CH_2Cl_2): ν_{CO}, 2004 s, 1972 m, 1932 s cm^{-1}. For **7**. Anal. Calcd for $C_{46}H_{34}Cl_2N_2O_4P_2Ru_2$: C, 54.50; H, 3.38; N, 2.76. Found: C, 54.13; H, 3.35; N, 2.69. ^{1}H NMR (25 °C, acetone-d_6, 400 MHz): δ 3.96 (s, 2 H), 5.09 (s, 2 H), 7.37 (m, 30 H). $^{31}P\{^1H\}$ (25 °C, acetone-d_6, 162 MHz): δ 29.91. IR (CH_2Cl_2): ν_{CO}, 2012 s, 1974 m, 1936 s cm^{-1}. For **9**. Anal. Calcd for $C_{54}H_{40}N_2O_4P_2Ru_2$: C, 62.07; H, 3.86; N, 2.68. Found: C, 62.10; H, 3.84; N, 2.58. ^{1}H NMR (25 °C, acetone-d_6, 400 MHz): δ 4.12 (s, 2 H), 7.53 (d, J = 8.4 Hz, 2 H), 8.02 (d, J = 8.4 Hz, 2 H), 7.00–7.17 (m, 34 H). $^{31}P\{^1H\}$ (25 °C, $CDCl_3$, 162 MHz): δ 29.73. IR (CH_2Cl_2): ν_{CO}, 2004 s, 1970 m, 1928 s cm^{-1}. For **10**. Anal. Calcd for $C_{46}H_{34}O_4P_2Ru_2S_2$: C, 56.44; H, 3.50. Found: C, 56.05; H, 3.53. ^{1}H NMR (25 °C, acetone-d_6, 400 MHz): δ 5.83 (m, 2 H), 6.03 (m, 2 H), 7.28 (m, 18 H), 7.40 (m, 12 H). $^{31}P\{^1H\}$ (25 °C, acetone-d_6, 162 MHz): δ 37.56. IR (CH_2Cl_2): ν_{CO}, 2016 s, 1982 m, 1950 s cm^{-1}.

Single-Crystal X-ray Diffraction Studies of 3, 4, and 12. Suitable single crystals were grown from CH_2Cl_2/hexane or CH_2Cl_2/Et_2O at room temperature and chosen for the single-crystal structure determination. Atomic coordinates and equivalent isotropic displacement coefficients for **3**, **4**, and **12** are listed in Tables 2–4, respectively. The X-ray diffraction data were measured on a four-circle diffractometer. Intensities of three standard reflections were monitored every hour or every 50 reflection throughout the data measurement. The variation was less than 2%. For **3**, the structure was solved by heavy-atom method and refined by a full-matrix least-square procedure using NRCVAX.[15] For **4**, the structure was solved by direct methods and refined by a full-matrix least-

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Table 5. Crystal Data for 3, 4, and 12

compound	**3**	**4**	**12**
formula	$C_{42}H_{42}B_2F_8N_4O_4P_2Ru_2$	$C_{18}H_{30}B_2F_4N_4O_4P_2Ru_2$	$C_{46}H_{34}O_4P_2Ru_2S_2$
fw	1104.50	804.2	978.98
color, habit	orange rhomboid	yellow column	yellow needle
diffractometer used	Nonius CAD4	Siemens R3m/V	Rigaku AFC7S
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, Å	20.292(6)	12.570(4)	11.151(1)
b, Å	17.223(7)	14.251(5)	21.302(2)
c, Å	15.186(3)	18.773(6)	10.183(2)
α, deg	90	90	93.65(1)
β, deg	113.324(18)	104.96(3)	113.43(1)
γ, deg	90	90	101.19(1)
V, Å^3	4873(3)	3251(9)	2151.2(6)
Z	4	4	2
D_{calcd}, g cm^{-3}	1.505	1.643	1.511
λ(Mo Kα), Å	0.709 30	0.710 73	0.710 69
F(000)	2216	1592	984
unit cell detn			
no. 2θ range, deg	25, 18−24	16, 13−23	25, 36−40
scan type	θ-2θ	θ-2θ	ω-2θ
2θ range, deg	2−45	2.5−50	6−50
h,k,l range	±21,18,16	±14,16,21	13,±25,±11
μ(Mo Kα), cm^{-1}	7.43	11.02	9.2
cryst size, mm	0.40 × 0.45 × 0.45	0.60 × 0.28 × 0.16	0.16 × 0.16 × 0.58
transm factor	0.944−1.000	0.888−0.939	0.933−1.000
temp, K	298	296	297
no. of measd reflns	3177	6280	7990
no. of unique reflns	3176	5729	7562
no. of obsd reflns (N_o)	2764 ($>2\sigma$)	3912 ($>3\sigma$)	6344 ($>3\sigma$)
R,[a] R_w[a]	0.045, 0.048	0.044, 0.044	0.038, 0.046
GOF[a]	2.27	1.53	2.81
no. of ref params (N_p)	290	362	485
weighting scheme	unit weights	$[\sigma^2(F_o) + 0.0003F_o^2]^{-1}$	$[\sigma^2(F_o)]^{-1}$
g(second ext coeff) × 10^4	0.65(9)	0	0
$(\Delta\varrho)_{max}$, e Å^{-3}	0.97	1.06	1.38
$(\Delta\varrho)_{min}$, e Å^{-3}	−0.62	−0.71	−1.04

[a] $R = [\sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

square procedure using SHELXTL-PLUS.[16] For **12**, the structure was solved by direct methods and refined by a full-matrix least-square procedure using TEXSAN.[17] The other essential details of single-crystal data measurement and refinement are givin in Table 5.

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Supplementary Material Available: Tables of complete bond lengths and angles, anisotropic displacement coefficients, and hydrogen coordinates for **3**, **4**, and **12** (17 pages). Ordering information is given on any current masthead page.

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