can be obtained from these activation parameters. The small ΔS^{*} indicates a unimolecular mechanism which may be dissociative or associative. One dissociative mechanism (Scheme II) involves the cleavage of a single Ga–As bond, rotation about the opposite (Ga–As) bond, and/or rotation around the adjacent (Ga–As) bond, and recombination. Reported values for the ΔH of dissociation of $Me_3Ga{\cdot}AsR_3$ adducts range from 8.2 to 14.6 kcal/mol.[20]

Exchange through an intermediate with five-coordinate gallium is another mechanistic possibility. One, or both exo-As atoms coordinates with the opposite Ga atom, and then one Ga–As bond to each five-coordinate gallium atom dissociates (Scheme III). Precedent for five-coordinate gallium exists.[21] One cannot distinguish between the mechanisms with the data available.

Acknowledgment. The financial support for this work by the Office of Naval Research is gratefully acknowledged.

Registry No. 1, 101860-04-2; 2, 109997-38-8; *cis*-3, 109997-39-9; *trans*-3, 110044-17-2; *cis*-4 (n = 2), 109997-40-2; *trans*-4 (n = 2), 110044-51-4; *cis*-5 (n = 3), 109997-41-3; *trans*-5 (n = 3), 110044-18-3; $GaBr_3$, 13450-88-9; $MeGaCl_2$, 6917-74-4; $PhGaCl_2$, 1073-46-7; Ga, 7440-55-3; As, 7440-38-2.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic temperature factors, and torsion angles (4 pages); a listing of observed and calculated structure amplitudes (32 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structures of (1,1′-Ruthenocenedithiolato-*S*,*S*′,*Ru*)(triphenylphosphine)nickel(II) and (1,1′-Metallocenedioxalato-*O*,*O*′,*Fe*-(or *Ru*))(triphenylphosphine)palladium(II): The Metal (Fe or Ru)–Metal (Pd or Ni) Dative Bond

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The reaction of 1,2,3-trithia[3](1,1′)ruthenocenophane with $Ni(PPh_3)_4$ in THF at room temperature gave $[Ru(\eta^5\text{-}C_5H_4S)_2]NiPPh_3$, although $[Fe(\eta^5\text{-}C_5H_4S)_2]NiPPh_3$ could not be obtained in a similar reaction between $Ni(PPh_3)_4$ and 1,2,3-trithia[3](1,1′)ferrocenophane. $[Fe(\eta^5\text{-}C_5H_4O)_2]PdPPh_3$ and $[Ru(\eta^5\text{-}C_5H_4O)_2]PdPPh_3$ were obtained by the reaction of the disodium salt of the metallocenediols (M = Fe or Ru) with $Pd(PPh_3)_2Cl_2$ in 28% yield. Palladium complexes could not be obtained via analogous methods. $[Ru(\eta^5\text{-}C_5H_4S)_2]NiPPh_3{\cdot}{}^1/_2C_6H_5CH_3$ crystallizes in the monoclinic space group $C2/c$ with $Z = 8$ and unit cell parameters a = 39.036 (7) Å, b = 10.463 (2) Å, c = 13.793 (4) Å, and β = 102.03 (2)°. The structure was refined to give R = 3.7% using 3840 independent reflections with $F_o \geq 2\sigma(F_o)$. $[Ru(\eta^5\text{-}C_5H_4O)_2]PdPPh_3$ crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and unit cell parameters a = 11.022 (6) Å, b = 14.872 (10) Å, c = 14.454 (5) Å, and β = 99.14 (3)°. The structure was refined to R = 3.9% using 3699 independent reflections with $F_o \geq 2\sigma(F_o)$. X-ray crystal data showed that $[Ru(\eta^5\text{-}C_5H_4O)_2]PdPPh_3$ and $[Fe(\eta^5\text{-}C_5H_4O)_2]PdPPh_3$ are isomorphous. The distances between the metal–metal and the large chemical shifts between the α- and β-ring protons in the ^1H NMR spectra of their complexes provide for appreciable evidence of Ru–Pd (or Fe–Pd and Ru–Ni) dative bonding.

Introduction

The coordination of the nonbonding d electrons (e_{2g} electrons) of the iron atom in the ferrocenophane nucleus to the vacant orbitals of another metal atom has been reported by Sano et al.[1] in [2](1,1′)ferrocenophane–metal halide. However, Whitesides et al.,[2] McCulloch et al.[3] and Butter et al.[4] reported no evidence of such kind of interaction between the iron atom and the platinum group metal atoms in compounds 1 and 2, respectively. Recently, Seyferth et al.[5] have attempted a synthesis of (1,1′-

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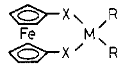
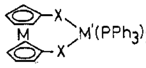


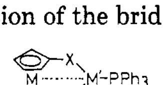
1: X = S(*i*-Bu), M = Pd, R = Cl
2a: X = PPh$_3$, M = Pt, R = *n*-Bu
b: X = PPh$_3$, M = Pd or Ni, R = Cl or Br

ferrocenedithiolato-*S*,*S*′)bis(triphenylphosphine)palladium(II) (**3a**). They obtained, however, a new type of



3a: M = Fe, X = S, M′ = Pd
b: M = Fe, X = S, M′ = Pt

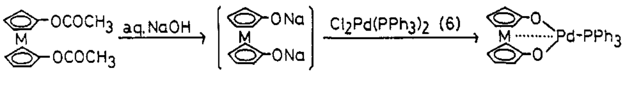
complex, (1,1′-ferrocenedithiolato-*S*,*S*′,*Fe*)(triphenylphosphine)palladium(II) (**4a**), instead of the expected complex **3a**. The ^{1}H NMR spectrum and X-ray analysis of **4a** suggest the presence of a dative bond between the iron atom of the ferrocene nucleus and palladium atom located at the 2-position of the bridge. The mono(phosphine) and bis(phosphine) complexes **4a** and **3a**, respectively, are intriguing compounds in that they may be closely related to catalytic and physiological activities.[6] In a previous paper,[7] we have reported on the systematic synthetic study of (1,1′-metallocenedichalcogenolato-*X*,*X*′,*M*)(triphenylphosphine)platinum(II) and -palladium(II) (X = S or Se; M = Fe or Ru) by the modified methods of Seyferth et al.[5] and X-ray analysis of the (1,1′-ferrocenedithiolato-*S*,*S*′,*Fe*)(triphenylphosphine)platinum(II) (**4b**). It was also determined that the reaction of 1,2,3-trichalcogena[3](1,1′)metallocenophane (M = Fe or Ru, X = S or Se) with tetrakis(triphenylphosphine)platinum(0) gave a mono(phosphine) complex (**4**) together with a bis(phosphine) complex (**3**), which then gave the corresponding mono(phosphine complex) **4** in quantitative yield by heating to 60 °C. The X-ray analysis of complex **4b** suggests the presence of the dative bond from the iron atom of the ferrocene nucleus to the platinum atom located at the 2-position of the bridge. The structure of **4b** is isostructural with the mono(phosphine) palladium complex **4a** noted by Seyferth et al.[5] We now wish to report the syntheses of (1,1′-ruthenocenedithiolato-*S*,*S*′,*Ru*)(triphenylphosphine)nickel(II) (**10**) and (1,1′-metallocenedioxalato-*O*,*O*′,*Fe*(or *Ru*))(triphenylphosphine)palladium(II) (**7a** and **7b**) along with the structures of these complexes as determined by X-ray crystallography.



4a: M = Fe, X = S, M′ = Pd
b: M = Fe, X = S, M′ = Pt

Results and Discussion

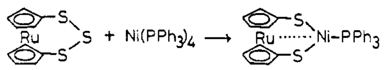
The preparation of (1,1′-ferrocenedioxalato-*O*,*O*′,*Fe*)(triphenylphosphine)palladium(II) (**7a**) was carried out as follows: the disodium salt of 1,1′-ferrocenediol (**5a**), which was prepared by hydrolysis of 1,1′-diacetoxyferrocene in 0.7% aqueous sodium hydroxide solution, was reacted with dichlorobis(triphenylphosphine)palladium(II) (**6**) in absolute tetrahydrofuran (THF) for 21 h at room temperature. The reaction mixture was treated by the usual methods and separated by alumina column chromatography to give a mono(phosphine) complex (**7a**) in 28% yield.



5a: M = Fe **7a**: M = Fe
b: M = Ru **b**: M = Ru

The corresponding mono(phosphine) complex **7b** of the ruthenocene derivative was obtained in 28% yield by the reaction of 1,1′-diacetoxyruthenocene (**5b**) with **6** according to the above method. However, the reaction of **5a** and/or **5b** with tetrakis(triphenylphosphine)platinum(0) and -palladium(0) gave no mono(phosphine) or bis(phosphine) complexes, although these reactions were carried out under many different conditions.

It has been reported that 1,2,3-trithia[3](1,1′)-metallocenophane reacts with tetrakis(triphenylphosphine)palladium(0) to give **4**.[5,7] This method has been used to synthesize (1,1′-ruthenocenedithiolato-*S*,*S*′,*Ru*)(triphenylphosphine)nickel(II) (**10**). In order to obtain **10**, tetrakis(triphenylphosphine)nickel(II) (**9**), which was obtained by the reaction of triphenylphosphine with bis(acetylacetonato)nickel(II) in the presence of triethylaluminum, was reacted with 1,2,3-trithia[3](1,1′)ruthenocenophane (**8**) in 50 mL of THF for 2 h at room temperature under nitrogen to give **10** in 26.5% yield. We were unable to obtain the bisphosphine complex. The corresponding mono- and bis(phosphine) complexes of ferrocene derivative also could not be isolated. Therefore, the ruthenium atom of the metallocene nucleus plays an important role in the mono(phosphine) complex formation in the nickel series.



8 **9** **10**

The structures of the new complexes were elucidated by their ^{1}H NMR and mass spectra and elemental analyses. For example, in the ^{1}H NMR spectrum of **7a**, two cyclopentadienyl ring protons of the ferrocene nucleus are found at δ 3.00 and 4.90 together with the multiplet peaks at δ 7.31–7.82 due to the phenyl group. The high- and low-field triplets were assigned to the α- and β-ring protons, respectively. Such a large splitting of the cyclopentadienyl ring protons was also observed in **7b** (δ 3.60 and 4.99) and **10** (δ 3.60 and 4.99). The large chemical shift differences (1.39–1.90 ppm) between the α- and β-ring protons of these complexes (**7a**, **7b**, and **10**) are mainly due to the anisotropic effect of the dative bond between the metal atom of the metallocene nucleus and the metal atom at the 2-position of the bridge on the α-ring protons, although other contributing factors could not be ruled out as previously described.[6]

Complexes **7b** and **10** were further characterized by X-ray analysis. Final atomic parameters and bond lengths and bond angles for **7b** and **10** are listed in Tables I, II, and III, respectively. However, complex **10** is isomorphous with that reported by Seyferth et al.;[5] therefore only the geometry around the Ni atom is discussed.

Perspective views of **7b** and **10** are shown in Figure 1. The average C–C bond lengths and C–C–C bond angles of the Cp rings of **7b** and **10** are in good agreement with the expected values. Also the average Ru···C and inter-ring C···C distances of the ruthenocene moiety of **7b** and **10** agree well with those for ruthenocene.[8] The dihedral angles between the two Cp rings are 9.8 (3) and 13.7 (2)°

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Table I. Fractional Atomic Coordinates (×10^4) with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
		7b		
Pd	9837.0 (4)	1842.1 (3)	7190.0 (3)	2.54
Ru	11889.2 (4)	2785.7 (3)	7811.4 (4)	2.82
O(1)	9191 (4)	3067 (3)	6741 (3)	4.24
O(2)	10914 (3)	786 (3)	7724 (3)	3.68
P	8055 (1)	1020 (1)	6912 (1)	2.33
C(1)	10223 (6)	3498 (4)	7063 (5)	4.14
C(2)	10568 (7)	3830 (4)	8017 (5)	4.25
C(3)	11735 (7)	4216 (5)	8067 (6)	5.33
C(4)	12165 (7)	4094 (5)	7215 (6)	5.10
C(5)	11253 (6)	3632 (5)	6599 (5)	4.25
C(6)	11891 (6)	1315 (4)	8035 (5)	3.70
C(7)	12124 (6)	1752 (5)	8906 (5)	4.01
C(8)	13228 (6)	2249 (5)	8942 (5)	4.77
C(9)	13656 (6)	2124 (5)	8062 (6)	5.47
C(10)	12832 (5)	1560 (4)	7503 (5)	3.68
C(11)	6672 (5)	1543 (4)	6269 (4)	2.51
C(12)	6524 (5)	2460 (4)	6338 (4)	3.25
C(13)	5434 (6)	2865 (4)	5945 (5)	4.26
C(14)	4493 (6)	2362 (5)	5471 (5)	4.13
C(15)	4626 (5)	1447 (5)	5388 (5)	3.95
C(16)	5714 (5)	1034 (4)	5784 (5)	3.45
C(21)	7590 (5)	710 (4)	8019 (4)	2.45
C(22)	6364 (5)	661 (4)	8158 (4)	3.39
C(23)	6074 (6)	394 (5)	9006 (5)	4.19
C(24)	6981 (6)	148 (4)	9727 (4)	3.69
C(25)	8185 (6)	203 (5)	9610 (4)	3.90
C(26)	8490 (5)	487 (5)	8773 (4)	3.63
C(31)	8200 (5)	−46 (4)	6319 (4)	2.57
C(32)	8541 (5)	−28 (5)	5443 (5)	3.76
C(33)	8737 (6)	−810 (6)	4988 (5)	5.05
C(34)	8592 (6)	−1625 (5)	5402 (5)	5.01
C(35)	8236 (7)	−1662 (4)	6253 (5)	4.96
C(36)	8025 (6)	−875 (4)	6727 (5)	3.68
		10		
Ru	3026.3 (1)	6265.3 (4)	2414.9 (3)	2.55
Ni	3485.9 (1)	4279.0 (6)	2035.3 (4)	2.63
S(1)	3256.8 (3)	3097.3 (12)	3033.3 (10)	3.74
S(2)	3713.0 (3)	5648.9 (12)	1186.6 (9)	3.55
P	3776.9 (3)	2691.8 (12)	1651.3 (9)	2.74
C(1)	2985 (1)	4379 (4)	3132 (3)	2.79
C(2)	3057 (1)	5370 (4)	3874 (3)	3.11
C(3)	2771 (1)	6232 (5)	3672 (3)	3.62
C(4)	2529 (1)	5830 (5)	2809 (3)	3.65
C(5)	2660 (1)	4699 (5)	2466 (3)	3.09
C(6)	3408 (1)	6717 (4)	1462 (3)	3.21
C(7)	3458 (1)	7567 (4)	2312 (4)	3.74
C(8)	3144 (1)	8277 (4)	2234 (4)	4.55
C(9)	2895 (1)	7845 (5)	1395 (4)	4.13
C(10)	3058 (1)	6889 (5)	927 (3)	3.54
C(11)	3510 (1)	1485 (4)	863 (3)	2.88
C(21)	4010 (1)	1850 (5)	2749 (3)	3.17
C(31)	4124 (1)	2988 (4)	960 (3)	2.92

[a] $B_{eq} = {}^4/_3\,(\beta_{11}/a^{*2} + \beta_{22}/b^{*2} + \beta_{33}/c^{*2})$.

Table II. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses of 7b

Bond Distances

Pd–Ru	2.692 (1)	C(11)–C(12)	1.380 (8)
Pd–O(1)	2.025 (4)	C(11)–C(16)	1.394 (8)
Pd–O(2)	2.045 (4)	C(12)–C(13)	1.383 (8)
Pd–P	2.295 (1)	C(13)–C(14)	1.370 (9)
O(1)–C(1)	1.325 (7)	C(14)–C(15)	1.375 (10)
O(2)–C(6)	1.351 (7)	C(15)–C(16)	1.388 (8)
P–C(11)	1.823 (5)	C(21)–C(22)	1.400 (6)
P–C(21)	1.815 (6)	C(21)–C(26)	1.392 (8)
P–C(31)	1.822 (6)	C(22)–C(23)	1.373 (9)
C(1)–C(2)	1.457 (10)	C(23)–C(24)	1.374 (9)
C(1)–C(5)	1.421 (9)	C(24)–C(25)	1.367 (8)
C(2)–C(3)	1.400 (9)	C(25)–C(26)	1.372 (9)
C(3)–C(4)	1.399 (11)	C(31)–C(32)	1.377 (8)
C(4)–C(5)	1.412 (10)	C(31)–C(36)	1.394 (8)
C(6)–C(7)	1.404 (10)	C(32)–C(33)	1.370 (10)
C(6)–C(10)	1.433 (8)	C(33)–C(34)	1.373 (11)
C(7)–C(8)	1.418 (9)	C(34)–C(35)	1.351 (10)
C(8)–C(9)	1.436 (11)	C(35)–C(36)	1.393 (9)
C(9)–C(10)	1.395 (10)		

Bond Angles

Ru–Pd–O(1)	82.7 (1)	C(8)–C(9)–C(10)	108.4 (4)
Ru–Pd–O(2)	82.4 (1)	C(6)–C(10)–C(9)	107.6 (4)
Ru–Pd–P	170.7 (1)	P–C(11)–C(16)	121.9 (3)
O(1)–Pd–O(2)	164.9 (1)	P–C(11)–C(12)	118.8 (3)
O(1)–Pd–P	100.1 (1)	C(12)–C(11)–C(16)	119.0 (4)
O(2)–Pd–P	94.9 (1)	C(11)–C(12)–C(13)	120.3 (5)
Pd–O(1)–C(1)	94.8 (2)	C(12)–C(13)–C(14)	120.5 (5)
Pd–O(2)–C(6)	93.6 (1)	C(13)–C(14)–C(15)	120.1 (5)
Pd–P–C(11)	118.9 (1)	C(14)–C(15)–C(16)	119.9 (5)
Pd–P–C(21)	109.5 (1)	C(11)–C(16)–C(15)	120.2 (4)
Pd–P–C(31)	114.2 (1)	P–C(21)–C(22)	123.6 (3)
C(11)–P–C(21)	103.1 (1)	P–C(21)–C(26)	119.0 (3)
C(11)–P–C(31)	105.0 (1)	C(22)–C(21)–C(26)	117.4 (4)
C(21)–P–C(31)	104.6 (1)	C(21)–C(22)–C(23)	120.7 (5)
O(1)–C(1)–C(5)	127.4 (6)	C(22)–C(23)–C(24)	120.6 (5)
O(1)–C(1)–C(2)	125.2 (5)	C(23)–C(24)–C(25)	119.6 (4)
C(2)–C(1)–C(5)	107.0 (4)	C(24)–C(25)–C(26)	120.4 (5)
C(1)–C(2)–C(3)	106.7 (4)	C(21)–C(26)–C(25)	121.3 (5)
C(2)–C(3)–C(4)	109.8 (5)	P–C(31)–C(32)	118.3 (3)
C(3)–C(4)–C(5)	108.1 (4)	P–C(31)–C(36)	122.9 (3)
C(1)–C(5)–C(4)	108.2 (4)	C(32)–C(31)–C(36)	118.8 (4)
O(2)–C(6)–C(7)	126.2 (5)	C(31)–C(32)–C(33)	120.8 (5)
O(2)–C(6)–C(10)	125.1 (5)	C(32)–C(33)–C(34)	120.2 (5)
C(7)–C(6)–C(10)	108.6 (4)	C(33)–C(34)–C(35)	120.2 (5)
C(6)–C(7)–C(8)	107.9 (4)	C(34)–C(35)–C(36)	120.6 (5)
C(7)–C(8)–C(9)	107.5 (4)	C(31)–C(36)–C(35)	119.4 (4)

for **7b** and **10**, respectively, and these values are smaller than those of **3a**[5] and **4b**[7] with the ferrocene unit. The differences probably reflect the longer inter-ring distance (3.64 Å) in ruthenocene than (3.32 Å) in ferrocene.[9] The Pd and Ni atoms of **7b** and **10** have a slightly distorted square-planar environment: the two S or O atoms occupy two trans positions, the Ru and P atoms occupy the other two trans positions, and the dihedral angles between the planes formed by S(1)–Pd–Ru and S(2)–Pd–P for **7b** and O(1)–Ni–Ru and O(2)–Ni–P for **10** are 8.9 and 7.8°, respectively. The angles between neighboring atoms in the distorted square-planar arrangement vary from 82.4 (1) to 100.1 (1)° for the palladium complex **7b** and from 86.6 (1) to 94.7 (1)° for the Ni complex **10**. The variation around Pd is rather similar to that of **4**[5] even though in **7b** the O atoms are attached to the Pd atom instead of the S atoms. The bond angles of C–S–Ni for **10** are 87.1 (2) and 86.0 (2)°, which are comparable to those of C–S–Pd in **4a** and C–S–Pt in **4b** in spite of the different metal at the 2-position of the bridge. The C–O–Pd bond angles for **7b** are 94.8 (2) and 93.6 (1)°. The obtuse angles for **7b** may be caused by the short bond length of the C–O bond, compared with that of the C–S bond.

A few heteronuclear complexes containing a Ru–Ni bond were reported.[10–12] In these oligonuclear complexes, the Ru–Ni bond length was 2.56–2.66 Å. The Ru–Ni bond length in complex **10** is 2.864 (1) Å and is rather longer than the observed values described above and the sum (2.41 Å) of the covalent radii[13] of Ru and Ni atoms. Similar to what was discussed in complexes **4a**[5] and **4b**,[7] the Ru–Ni

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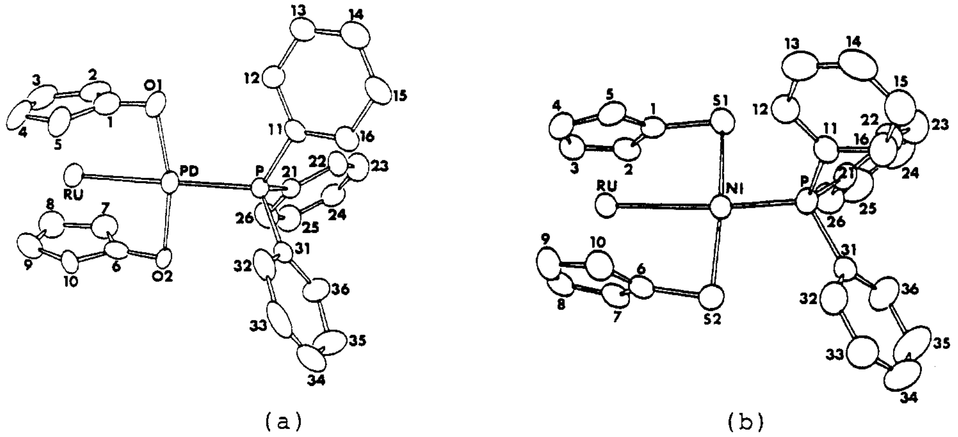

(a) (b)

Figure 1. ORTEP drawings of molecules with atomic numbering scheme of (a) **7b** and (b) **10**.

Table III. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses of 10

Bond Distances			
Ru-Ni	2.864 (1)	C(1)-C(2)	1.444 (6)
Ni-S(1)	2.176 (1)	C(1)-C(5)	1.441 (5)
Ni-S(2)	2.155 (1)	C(2)-C(3)	1.417 (6)
Ni-P	2.140 (1)	C(3)-C(4)	1.419 (6)
S(1)-C(1)	1.734 (4)	C(4)-C(5)	1.410 (7)
S(2)-C(6)	1.732 (4)	C(6)-C(7)	1.453 (6)
P-C(11)	1.841 (4)	C(6)-C(10)	1.421 (6)
P-C(21)	1.823 (5)	C(7)-C(8)	1.416 (6)
P-C(31)	1.837 (4)	C(8)-C(9)	1.422 (7)
		C(9)-C(10)	1.413 (7)
Bond Angles			
Ru-Ni-S(1)	86.6 (1)	S(1)-C(1)-C(5)	127.0 (3)
Ru-Ni-S(2)	87.8 (1)	S(1)-C(1)-C(2)	125.3 (2)
Ru-Ni-P	173.4 (1)	C(2)-C(1)-C(5)	107.6 (3)
S(1)-Ni-S(2)	172.4 (1)	C(1)-C(2)-C(3)	106.7 (2)
S(1)-Ni-P	91.4 (1)	C(2)-C(3)-C(4)	109.6 (3)
S(2)-Ni-P	94.7 (1)	C(3)-C(4)-C(5)	107.9 (2)
Ni-S(1)-C(1)	87.1 (2)	C(1)-C(5)-C(4)	108.2 (3)
Ni-S(2)-C(6)	86.0 (2)	S(2)-C(6)-C(7)	126.1 (2)
Ni-P-C(11)	114.5 (1)	S(2)-C(6)-C(10)	126.7 (3)
Ni-P-C(21)	111.6 (1)	C(7)-C(6)-C(10)	107.1 (2)
Ni-P-C(31)	118.9 (1)	C(6)-C(7)-C(8)	106.9 (2)
C(11)-P-C(21)	106.4 (1)	C(7)-C(8)-C(9)	109.3 (3)
C(11)-P-C(31)	101.3 (1)	C(8)-C(9)-C(10)	107.3 (2)
C(21)-P-C(31)	102.6 (1)	C(6)-C(10)-C(9)	109.2 (3)

bond in **10** is required for obtaining a stable electron configuration (16-electron) around the Ni(II) atom. Therefore, there is most likely a weak dative bond from the Ru atom to the Ni(II) atom. Since Ru-Ru separations of more than 2.8 Å were observed in oligonuclear ruthenium complexes[14] and Ni-Ni distances of more than 2.8 Å are known in dinuclear[15] and trinuclear nickel complexes,[16] the 2.864 Å of the Ru-Ni bonding does not seem to be unreasonable.

The Ni-S bond distances (2.176 (1) and 2.155 (1) Å) in **10** are identical with those (2.16 Å) of the nickel thiolato complexes,[17] while the Ni-P bond distance (2.140 Å) is somewhat shorter than that (2.175-2.196 Å) in the nickel(II) phosphine complex.[18-20] Apparently, this shortening of the Ni-P bond compensates for the lengthening of the Ru-Ni bond trans to the Ni-P bond.

For the complex **7b**, the Ru-Pd bond length (2.692 (1) Å) is somewhat longer than that (2.660 (1) Å) in the only complex reported containing a Ru-Pd bond.[21] It also is longer than the sum (2.53 Å) of the covalent radii of Ru and Pd atoms. Arguments analogous to those presented above suggest that this Ru-Pd bond also is a dative bond from a Ru atom to a Pd(II) atom. The difference between the observed distance and the sum of the covalent radii of the corresponding atoms is noteworthy. The difference (0.162 Å) in **7b** is much smaller than those in the other complexes (0.428 Å in **4a**, 0.466 Å in **4b**, and 0.454 Å in **10**), perhaps in part because the C-O bond is shorter than the C-S bond and as a result of steric effects of the bridging group holding the two metals apart. The Ru-Pd bond in **7b** also may be stronger than the other metal-metal dative bonds described above because the Pd-P bond length (2.295 (1) Å) in **7b** is longer than that (2.241 (1) Å) in **4a**. The Pd-O bond distances (2.028 (4) and 2.045 (4) Å) in **7b** match those (2.028 and 2.039 Å) in (tetrachlorocatecolato-*O*,*O*)bis(triphenylphosphine)palladium(II).[22] In spite of the formation of the dative bonds between the ruthenium atom and the Pd (or Ni) atom in **7b** and **10**, no variation of the Pd-O and Ni-S bond lengths can be observed, although in the case of ferrocene derivatives **4a** and **4b** the formation of the dative bonds between Fe and Pt (or Fe and Pd) is apparently reflected in the Pt-S (or Pd-S) distances as described in a previous paper.[7] This may be attributed to the longer inter-ring distance in the ruthenocene nucleus than in the ferrocene nucleus, although we cannot rule out other effects.

Experimental Section

The melting and decomposition points were uncorrected. The electronic spectra were measured on a Hitachi 330 spectrometer. The ^{1}H NMR spectra were obtained on a JEOL FX-90Q spectrometer, TMS being chosen as an internal standard.

Materials. 1,2,3-Trithia[3](1,1′)ferrocenophane,[23] 1,2,3-trithia[3](1,1′)ruthenocenophane,[24] 1,1′-diacetoxyruthenocene,[25] and 1,1′-diacetoxyferrocene[26] were prepared according to the previously

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reported methods. Dichlorobis(triphenylphosphine)palladium(0)[27] and tetrakis(triphenylphosphine)nickel(0)[28] were prepared according to the literatures. Other reagents employed were commercially available or were prepared by the usual method. Solvents were dried in appropriate methods and then purified by distillation under nitrogen.

[Fe(η^5-C_5H_4O)$_2$]PdPPh$_3$ (7a). To a solution of 0.7% aqueous sodium hydroxide solution was added **5a** (0.711 g, 2.35 mmol), and the mixture was stirred for 1 h at 80 °C under nitrogen. After the mixture had been cooled to room temperature, a suspension of **6** (1.76 g, 2.52 mmol) in 50 mL of THF was added at once and then the reaction mixture was stirred for 21 h at room temperature under nitrogen. The reaction mixture was extracted with ethyl ether. The extract was evaporated in vacuo. The residue was chromatographed on a neutral activated alumina by elution with benzene. The second band gave red oil that was recrystallized from hexane–benzene to give **7a** in 28% yield: mp 228.5–230.5 °C; MS (70 eV), *m/e* 584 (M^+); ^{1}H NMR (in $CDCl_3$) δ 3.00 (t, J = 2.1 Hz, 4 H), 4.90 (t, J = 2.1 Hz, 4 H), 7.31–7.82 (m, 15 H); UV (in THF) λ_{max} (ϵ) 261 (13 300), 284 (18 700), 345 (6630), 509 nm (122 M^{-1} cm^{-1}). Anal. Calcd for $C_{28}H_{23}FeO_2PPd \cdot C_6H_6$: C, 61.61; H, 4.41. Found: C, 61.57; H, 4.60.

[Ru(η^5-C_5H_4O)$_2$]PdPPh$_3$ (7b). The reaction of **5b** with **6** was carried out in a manner analogous to that discribed above: yield 28%; mp 244.0–245.0 °C; MS (70 eV), *m/e* 629 (M^+); ^{1}H NMR (in $CDCl_3$) δ 3.60 (t, J = 2.0 Hz, 4 H), 4.99 (t, J = 2.0 Hz, 4 H), 7.20–7.82 (m, 15 H); UV (in THF) λ_{max} (ϵ) 261 (13 300), 312 (17 500), 368 (3360), 450 nm (389 M^{-1} cm^{-1}). Anal. Calcd for $C_{28}H_{23}O_2PPdRu$: C, 53.42; H, 3.66. Found: C, 53.62; H, 4.00.

[Ru(η^5-C_5H_4S)$_2$]NiPPh$_3$ (10). A mixture of **9** (0.33 g, 3.70 mmol and **8** (0.315 g, 0.968 mmol) in 50 mL of THF was stirred for 2 h at room temperature under nitrogen, and then the reaction mixture was evaporated in vacuo. The residue was chromatographed on silica gel (chloroform as eluent). The red-purple fraction was concentrated in vacuo, and the residue was recrystallized from hexane–toluene to give **10** in 26.5% yield: mp 230 °C; ^{1}H NMR (in $CDCl_3$) δ 3.64 (t, J = 2.0 Hz, 4 H), 5.06 (t, J = 2.0 Hz, 4 H), 7.30–7.80 (m, 15 H); UV (in THF) λ_{max} (ϵ) 288 (11 000), 333 (12 000), 512 nm (700 M^{-1} cm^{-1}). Anal. Calcd for $C_{28}H_{23}S_2PRuNi \cdot {}^1/_2C_6H_5CH_3$: C, 57.27; H, 4.09. Found: C, 57.53; H, 4.38.

X-ray Crystallography of 7b and 10. Crystals of dimensions 0.35 × 0.3 × 0.2 for **7b** and 0.3 × 0.3 × 0.15 for **10**, obtained from CH_2Cl_2/toluene/hexane, were used for the X-ray analysis. Lattice constants were determined by least-squares fit of angular settings of 20 reflections within the range $15 \leq 2\theta \leq 30°$. Intensity data were obtained on a Rigaku AFC-5R diffractometer equipped with graphite-monochromatized Mo Kα radiation and using the $\theta \leq 2\theta$ scan technique ($2\theta \leq 50°$). During data collection three standards, measured before every 200 reflections, indicated no systematic variation of intensity with time. Of 4128 and 4799 independent reflections measured, only 3699 and 3840 for **7b** and **10**, respectively, were considered as observed on the basis of the criterion $F_o \geq 2\sigma(F_o)$. All intensities were corrected for Lorentz and polarization effects but not for absorption.

Crystal data for 7b: $C_{28}H_{23}PRuPd$; M_w 630.0; monoclinic, $P2_1/n$; a = 11.022 (6) Å, b = 14.872 (10) Å, c = 14.454 (5) Å, β = 99.14 (3)°; U = 2339.2 A^3; Z = 4; ρ = 1.79 g cm^{-3}; μ(Mo Kα) = 15 cm^{-1}; T = 297 K.

Crystal data for 10: $C_{28}H_{23}PS_2RuNi \cdot {}^1/_2C_6H_5CH_3$; M_w 660.5; monoclinic, $C2/c$; a = 39.036 (7) Å, b = 10.463 (2) Å, c = 13.793 (4) Å, β = 102.03 (2)°; U = 5509.7 Å^3; Z = 8; ρ = 1.60 g cm^{-3}; μ (Mo Kα) = 14.5 cm^{-1}; T = 297 K.

Both structures of **7b** and **10** were solved by the heavy-atom technique and refined by block-diagonal least-squares methods. Positions of the hydrogen atoms were estimated from standard geometry. The final refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered R values to 0.039 (R_w = 0.040, $w = 1/\sigma(F_o)$) and 0.037 (R_w = 0.030, $w = 1/\sigma(F_o)$) for **7b** and **10**, respectively. The goodnesses of fit values were 2.91 and 4.32, and maximum and minimum heights in the final difference Fourier syntheses were +0.8, –0.8 and +0.5, –0.4 e A^{-3}, located within 1.4 Å from the Pd and Ni atoms for **7b** and **10**, respectively. Maximum and average shifts in the final cycle of refinements were 0.33, 0.05 and 0.71, 0.08 of the corresponding standard deviations for **7b** and **10**, respectively. Anomalous dispersion corrections were applied to the scattering factors of Ni, Pd, Ru, S, and P.[29]

Registry No. 5a, 109889-99-8; **5b**, 109890-00-8; **6**, 28966-81-6; **7a**, 109889-97-6; **7b**, 109889-98-7; **8**, 91607-76-0; **9**, 15133-82-1; **10**, 109890-01-9; $(CpOH)_2Fe$, 109890-02-0; $(CpOH)_2Ru$, 109890-03-1; $(CpOAc)_2Fe$, 12093-94-6; $(CpOAc)_2Ru$, 101178-15-8.

Supplementary Material Available: Lists of H-atom parameters and anisotropic temperature factors for **7b** (2 pages); a listing of structure factors (23 pages). Ordering information is given on any current masthead page.

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