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Synthesis of $TiRu_2$ Heterobimetallic and TiRuM (M = Rh, Ir, Pd, Pt) Heterotrimetallic Sulfido Clusters from a Hydrosulfido-Bridged Titanium−Ruthenium Complex

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Treatment of the hydrosulfido-bridged titanium−ruthenium heterobimetallic complex $[Cp_2Ti(\mu_2\text{-SH})_2RuCl(\eta^5\text{-}C_5Me_5)]$ (**1**; Cp = η^5-C_5H_5) with an excess of triethylamine followed by addition of $[RuCl_2(PPh_3)_3]$ and $[\{(cod)M\}_2(\mu_2\text{-Cl})_2]$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) led to the formation of the $TiRu_2$ and TiRuM mixed-metal sulfido clusters $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Ru(PPh_3)_2\}(\mu_3\text{-S})_2(\mu_2\text{-Cl})_2]$ (**3**) and $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{M(cod)\}(\mu_3\text{-S})_2(\mu_2\text{-Cl})]$ (M = Rh (**4a**), Ir (**4b**)), respectively. On the other hand, the reactions of **1** with $[M(PPh_3)_4]$ (M = Pd, Pt) afforded the TiRuM trinuclear clusters $[(CpTiCl)\{(\eta^5\text{-}C_5Me_5)Ru\}\{M(PPh_3)_2\}(\mu_3\text{-S})(\mu_2\text{-S})(\mu_2\text{-H})]$ (M = Pd (**5a**), Pt (**5b**)) with an unprecedented $M_3(\mu_3\text{-S})(\mu_2\text{-S})$ core. The detailed structures of these triangular clusters **3**−**5** have been determined by X-ray crystallography. Crystal data: **3**, triclinic, $P\bar{1}$, $a = 12.448(4)$ Å, $b = 12.773(4)$ Å, $c = 17.270(4)$ Å, $\alpha = 100.16(2)°$, $\beta = 99.93(2)°$, $\gamma = 114.11(3)°$, $V = 2373(1)$ Å^3, $Z = 2$; **4a**, triclinic, $P\bar{1}$, $a = 7.714(2)$ Å, $b = 11.598(3)$ Å, $c = 14.802(4)$ Å, $\alpha = 80.46(2)°$, $\beta = 82.53(2)°$, $\gamma = 71.47(2)°$, $V = 1234.0(6)$ Å^3, $Z = 2$; **4b**, triclinic, $P\bar{1}$, $a = 7.729(1)$ Å, $b = 11.577(2)$ Å, $c = 14.766(3)$ Å, $\alpha = 80.14(1)°$, $\beta = 82.71(1)°$, $\gamma = 71.55(1)°$, $V = 1231.1(4)$ Å^3, $Z = 2$; **5a**, monoclinic, $P2_1/c$, $a = 11.259(4)$ Å, $b = 16.438(4)$ Å, $c = 26.092(5)$ Å, $\beta = 102.23(3)°$, $V = 4719(2)$ Å^3, $Z = 4$; **5b**, monoclinic, $P2_1/n$, $a = 11.369(2)$ Å, $b = 16.207(3)$ Å, $c = 26.116(2)$ Å, $\beta = 102.29(1)°$, $V = 4701(1)$ Å^3, $Z = 4$.

Introduction

Significant progress has been achieved in the methodology of cluster synthesis during the last two decades. A substantial part of this progress has been concerned with the development of a rational strategy to control the structures and metal composition of the clusters that are produced.[1−3] Heterotrimetallic clusters with a triangular array of three distinct metal atoms have been a major subject of systematic investigation to confirm the efficiency of these rational approaches.[4] Stone and coworkers have demonstrated that stepwise accumulation of two distinct metal fragments onto the mononuclear alkylidyne complexes provides a general route to heterotrimetallic clusters with a μ_3-alkylidyne ligand.[5,6] Substitution of an anionic ligand in diphosphine-bridged heterodinuclear complexes by anionic metal complexes has been developed by Braunstein and coworkers.[7] A metal exchange reaction, i.e., replacement of one metal vertex in a trinuclear cluster by its isolobal metal fragment, gives an additional class of heterotrimetallic clusters.[8−10] However, metals involved in these systematic studies have been limited to group 6−11 metals.[4]

In the course of our extensive studies on sulfur-bridged complexes of noble metals,[11,12] our research group has established the synthetic utility of the hydrosulfido-bridged homodinuclear complexes $[(\eta^5\text{-}C_5Me_5)MCl(\mu_2\text{-SH})_2MCl(\eta^5\text{-}C_5Me_5)]$ (M = Ru, Rh, Ir) for a variety of sulfido clusters.[13−20] For example, reactions of these hydrosulfido complexes with

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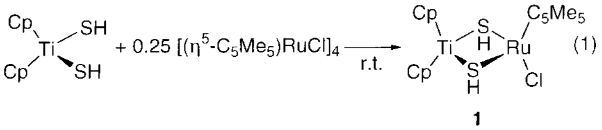
heterometallic compounds led to the formation of a series of heterobimetallic sulfido clusters with triangular[14−18] and pentanuclear bow-tie cores.[17] With the aim of extending this finding to the chemistry of early transition metals, we have recently synthesized the hydrosulfido-bridged heterodinuclear complex $[Cp_2Ti(\mu_2\text{-}SH)_2RuCl(\eta^5\text{-}C_5Me_5)]$ (**1**) by the reaction of $[Cp_2Ti(SH)_2]$ and $[\{(\eta^5\text{-}C_5Me_5)Ru\}_4(\mu_3\text{-}Cl)_4]$ (eq 1).[21,22] Subsequent



self- or crossed-condensation reactions of **1** give rise to the formation of the mixed-metal cubane-type sulfido clusters $[(CpTi)_2\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_3\text{-}S)_4]$ (**2**)[21,22] and $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu_3\text{-}S)_4]$,[23] which represent still rare examples of mixed-metal sulfido clusters containing titanium.

When attention is directed to the stepwise synthesis of heterotrimetallic triangular sulfido clusters containing titanium, the formation of **1** can be viewed as the first step of the cluster synthesis by using hydrosulfido ligands as a template for aggregation of three distinct metal fragments. The present study addresses the final step of this bridge-assisted nuclearity expansion to give trinuclear sulfido clusters containing the metal atoms of the two extreme ends of the d block in the periodic table. These trinuclear clusters have a $TiRuMS_2$ core composition in common; however, the core structures depend strongly upon the incoming metals M.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Solvents were dried by refluxing over Na/benzophenone ketyl (THF, toluene, benzene, and hexanes) or P_2O_5 (dichloromethane) and distilled before use. Triethylamine was distilled from KOH. Complex **1** was prepared according to the literature.[22] ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL EX-270 and LA-400 spectrometers. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer.

Preparation of $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Ru(PPh_3)_2\}(\mu_3\text{-}S)_2(\mu_2\text{-}Cl)_2]$ (3). Triethylamine (400 μL, 2.9 mmol) was added to a THF (20 mL) solution of **1** (277.5 mg, 0.538 mmol) at −78 °C. To the resultant deep violet solution was added $[RuCl_2(PPh_3)_3]$ (516.1 mg, 0.538 mmol) at this temperature, and the mixture was slowly warmed to room temperature with stirring. After removal of the solvent in vacuo, the resultant dark red residue was extracted with benzene (10 mL). The extract was evaporated to dryness and recrystallized from THF−hexanes (10 mL/40 mL). The dark brown crystals that formed were filtered off, washed with hexanes (3 mL × 2), and dried in vacuo (378.4 mg, 63%). ^1H NMR (C_6D_6): δ 7.8−6.9 (m, 30H, Ph), 6.40 (s, 5H, C_5H_5), 1.48 (s, 15H, C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 33.6 (s). Anal. Calcd for $C_{51}H_{50}Cl_2P_2Ru_2S_2Ti$: C, 55.19; H, 4.54. Found: C, 55.47; H, 4.75.

Preparation of $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Rh(cod)\}(\mu_3\text{-}S)_2(\mu_2\text{-}Cl)]$ (4a). Triethylamine (340 μL, 2.45 mmol) was added to a THF (25 mL) solution of **1** (249.0 mg, 0.483 mmol) at −78 °C. To the resultant deep violet solution was added $[\{(cod)Rh\}_2(\mu_2\text{-}Cl)_2]$ (119.9 mg, 0.243 mmol) at this temperature, and the mixture was slowly warmed to room temperature with stirring. The resultant dark green solution was evaporated to dryness and extracted with toluene (30 mL). Addition of hexanes (40 mL) to the concentrated extract afforded dark brown crystals of **4a**, which were collected by filtration and dried in vacuo (128.6 mg, 40%). ^1H NMR (C_6D_6): δ 6.48 (s, 5H, C_5H_5), 4.51, 4.35, 2.21, 2.06 (br s, 2H each, cod), 1.85 (s, 15H, C_5Me_5). The other methylene resonances (4H) for the cod ligand are masked by the C_5Me_5 singlet. Anal. Calcd for $C_{23}H_{32}ClRhRuS_2Ti$: C, 41.86; H, 4.89. Found: C, 41.46; H, 5.01.

Preparation of $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Ir(cod)\}(\mu_3\text{-}S)_2(\mu_2\text{-}Cl)]$ (4b). Triethylamine (70 μL, 0.50 mmol) was added to a THF (5 mL) solution of **1** (49.9 mg, 0.0967 mmol) at −78 °C. To the resultant deep violet solution was added $[\{(cod)Ir\}_2(\mu_2\text{-}Cl)_2]$ (31.9 mg, 0.0475 mmol) at this temperature, and the mixture was slowly warmed to room temperature with stirring. The resultant dark green solution was evaporated to dryness and extracted with toluene (12 mL). Addition of hexanes (18 mL) to the concentrated extract afforded dark brown crystals of **4b**, which were collected by filtration and dried in vacuo (22.6 mg, 32%). ^1H NMR (C_6D_6): δ 6.46 (s, 5H, C_5H_5), 4.33, 3.80, 2.25, 2.01 (br s, 2H each, cod), 1.81 (s, 15H, C_5Me_5). The other methylene resonances (4H) for the cod ligand are masked by the C_5Me_5 singlet. Anal. Calcd for $C_{23}H_{32}ClIrRuS_2Ti$: C, 36.87; H, 4.30. Found: C, 36.69; H, 4.45.

Preparation of $[(CpTiCl)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Pd(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ (5a). Triethylamine (1.4 mL, 10 mmol) was added to a THF (100 mL) solution of **1** (1.039 g, 2.01 mmol) at −78 °C. To the resultant deep violet solution was added $[Pd(PPh_3)_4]$ (2.323 g, 2.01 mmol) at this temperature, and the mixture was slowly warmed to room temperature with stirring. The resultant violet solution was evaporated to dryness. Extraction with benzene and subsequent recrystallization from dichloromethane−hexanes (5 mL/45 mL) afforded deep violet crystals of **5a** along with an off-white powder; the latter was removed by decantation with hexanes. Yield: 1.426 g (66%). ^1H NMR (C_6D_6): δ 7.7−6.7 (m, 30H, Ph), 6.11 (s, 5H, C_5H_5), 1.59 (s, 15H, C_5Me_5), −11.92 (dd, 1H, $^2J_{PH}$ = 114.7, 4.9 Hz, RuPdH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 12.7, 8.2 (d, 1P each, $^2J_{PP}$ = 64.9 Hz). Anal. Calcd for $C_{51}H_{51}ClP_2PdRuS_2Ti$: C, 56.67; H, 4.76. Found: C, 56.33; H, 4.85.

Preparation of $[(CpTiCl)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Pt(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ (5b). A mixture of **1** (255.3 mg, 0.495 mmol) and $[Pt(PPh_3)_4]$ (615.6 mg, 0.495 mmol) in THF (40 mL) was stirred at room temperature for 22 h. After removal of the solvent, the resultant dark brown residue was recrystallized from dichloromethane−hexanes (5 mL/45 mL). Repeated recrystallization (three times) afforded **5b** as dark brown crystals (23.7 mg, 4%). ^1H NMR (C_6D_6): δ 7.7−6.7 (m, 30H, Ph), 6.20 (s, 5H, C_5H_5), 1.58 (s, 15H, C_5Me_5), −11.54 (dd with ^{195}Pt satellites, 1H, $^2J_{PH}$ = 119.6, 14.6 Hz, $^1J_{PtH}$ = 666.2 Hz, RuPtH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 10.9 (d with ^{195}Pt satellites, 1P, $^2J_{PP}$ = 21.6 Hz, $^1J_{PtP}$ = 3659.9 Hz), 8.1 (d with ^{195}Pt satellites, 1P, $^2J_{PP}$ = 21.6 Hz, $^1J_{PtP}$ = 3415.3 Hz). Anal. Calcd for $C_{51}H_{51}ClP_2PtRuS_2Ti$: C, 52.38; H, 4.40. Found: C, 52.03; H, 4.46.

X-ray Diffraction Studies. Single crystals suitable for X-ray analyses were sealed in glass capillaries under an inert atmosphere and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a graphite-monochromatized Mo Kα source (λ = 0.710 69 Å). Orientation matrixes and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections with $25° < 2\theta < 40°$. The data collection was performed at 294 K using the $\omega-2\theta$ scan (for **3**, **4a**, and **4b**) or ω-scan (for **5a** and **5b**) technique at a rate of 32° min^{-1} to a maximum 2θ value of 55°. The intensities of 3 check reflections were monitored every 150 reflections during data collection, which revealed no significant decay. Intensity data were corrected for Lorentz−polarization effects and for absorption (ψ scans). Details of crystal and data collection parameters are summarized in Table 1.

Structure solution and refinements were carried out by using the teXsan program package.[24] The heavy-atom positions were determined by a Patterson method program (DIRDIF92-PATTY[25]), and the remaining non-hydrogen atoms were found by subsequent Fourier

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Table 1. X-ray Crystallographic Data for **3**, **4a**, **4b**, **5a**, and **5b**

	3	**4a**	**4b**	**5a**	**5b**
formula	$C_{51}H_{50}Cl_2P_2Ru_2S_2Ti$	$C_{23}H_{32}ClRhRuS_2Ti$	$C_{23}H_{32}ClIrRuS_2Ti$	$C_{51}H_{51}ClP_2PdRuS_2Ti$	$C_{51}H_{51}ClP_2PtRuS_2Ti$
fw	1109.97	659.95	749.27	1080.85	1169.54
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	12.448(4)	7.714(2)	7.729(1)	11.259(4)	11.369(2)
b, Å	12.773(4)	11.598(3)	11.577(2)	16.438(4)	16.207(3)
c, Å	17.270(4)	14.802(4)	14.766(3)	26.092(5)	26.116(2)
α, deg	100.16(2)	80.46(2)	80.14(1)	90	90
β, deg	99.93(2)	82.53(2)	82.71(1)	102.23(3)	102.29(1)
γ, deg	114.11(3)	71.47(2)	71.55(1)	90	90
V, Å^3	2373(1)	1234.0(6)	1231.1(4)	4719(2)	4701(1)
Z	2	2	2	4	4
ρ_{calcd}, g cm^{-3}	1.553	1.776	2.021	1.521	1.652
ρ_{obsd}, g cm^{-3}	1.56	1.78		1.53	1.64
μ(Mo Kα), cm^{-1}	10.95	18.65	66.15	11.06	36.87
R_{int}	0.045	0.016	0.018	0.023	0.094
R^a	0.045	0.042	0.038	0.042	0.050
$R_w{}^b$	0.044	0.054	0.053	0.046	0.054

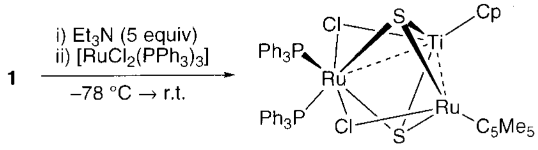
[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, $w = [\sigma_c{}^2(F_o) + p^2F_o{}^2/4]^{-1}$ (p = 0.020 (**3** and **5b**), 0.025 (**4a**), 0.030 (**4b**), 0.015(**5a**)) with $\sigma_c(F_o)$ from counting statistics.

syntheses. The C_5Me_5 carbon atoms in **4a**, **4b**, **5a**, and **5b** were found to be disordered and refined isotropically as rigid groups with occupancies of 60 and 40% (in **4a** and **4b**), or 55 and 45% (in **5a** and **5b**). All non-hydrogen atoms except for these carbon atoms were refined anisotropically by full-matrix least-squares techniques (based on F). The hydrido hydrogen atoms in **5a** and **5b** were found in the final difference Fourier maps. All other hydrogen atoms except for those in the disordered C_5Me_5 groups in **4a**, **4b**, **5a**, and **5b** were placed at calculated positions; these hydrogen atoms were included in the final stages of refinements with fixed parameters. The atomic scattering factors were taken from ref 26, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 27.

Results and Discussion

Synthesis and Structure of TiRu$_2$ Cluster 3. We have already demonstrated that the hydrosulfido-bridged homodinuclear complexes $[(\eta^5\text{-}C_5Me_5)MCl(\mu_2\text{-}SH)_2MCl(\eta^5\text{-}C_5Me_5)]$ (M = Ru, Ir) react with $[RuH_2(PPh_3)_4]$ to afford the sulfido-capped trinuclear clusters $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_3\text{-}S)_2(\mu_2\text{-}H)RuCl(PPh_3)_2]$[19] and $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2(\mu_3\text{-}S)_2RuCl_2(PPh_3)]$,[18] respectively. On the basis of these findings, we first attempted the reaction of the hydrosulfido-bridged titanium−ruthenium complex **1** with $[RuH_2(PPh_3)_4]$. Isolated from the reaction mixture were, however, the cubane-type cluster $[(CpTi)_2\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_3\text{-}S)_4]$ (**2**) and $[CpRuH(PPh_3)_2]$.[28] Although the detailed reaction mechanism is obscure, formation of the latter complex may be explained by the reaction of $[RuH_2(PPh_3)_4]$ with cyclopentadiene, which is eliminated from **1**. Indeed, base-induced elimination of cyclopentadiene and HCl from **1** to give **2** has already been established.[21,22] The reaction of **1** with $[RuCl_2(PPh_3)_3]$ was also attempted, which afforded a complex mixture containing $[Cp_2TiCl_2]$ and unidentified products.

At this juncture, we turned our attention to a coordinatively unsaturated species derived from the hydrosulfido complex **1**. We have previously observed that a dark reddish brown solution of **1** turns deep violet upon treatment with triethylamine at −78 °C; the reaction gives the dark reddish brown Ti_2Ru_2 cubane-type cluster **2** as the final product.[21,22] Although this violet species remains uncharacterized, it is probable that a coordinatively unsaturated species such as $[Cp_2Ti(\mu_2\text{-}S)(\mu_2\text{-}SH)Ru(\eta^5\text{-}C_5Me_5)]$ and $[CpTi(\mu_2\text{-}S)_2Ru(\eta^5\text{-}C_5Me_5)]$ is generated at this stage. Formation of the corresponding coordinatively unsaturated intermediates $[(\eta^5\text{-}C_5Me_5)M(\mu_2\text{-}S)_2M(\eta^5\text{-}C_5Me_5)]$ (M = Ru, Ir) from $[(\eta^5\text{-}C_5Me_5)MCl(\mu_2\text{-}SH)_2MCl(\eta^5\text{-}C_5Me_5)]$ and triethylamine is deduced from the ^{1}H NMR spectrum of the reaction mixture[15,29] or a trapping experiment with alkynes.[19] These observations prompted us to examine the reaction of this violet solution with mononuclear ruthenium complexes at −78 °C. When the mixture of the violet solution and $[RuCl_2(PPh_3)_3]$ was warmed to room temperature, the TiRu$_2$ cluster $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Ru(PPh_3)_2\}(\mu_3\text{-}S)_2(\mu_2\text{-}Cl)_2]$ (**3**) was obtained in 63% yield (eq 2). The ^{1}H NMR spectrum of **3** exhibits signals ascribed to the Cp, C_5Me_5, and PPh_3 protons in an intensity ratio of 5:15:30, suggesting that a $Ru(PPh_3)_2$ fragment is incorporated into the $TiRuS_2$ core derived from **1**. No signals attributable to hydrosulfido or hydrido resonances are observed. The integral ratio also indicates that one of the Cp ligands in **1** has been lost during the reaction, as in the transformation of **1** into the cubane-type cluster **2**. On the other hand, the reaction using $[RuH_2(PPh_3)_4]$ instead of $[RuCl_2(PPh_3)_3]$ afforded a complex mixture containing $[CpRuH(PPh_3)_2]$ and **2**.



(2)

3

The trinuclear structure of **3** has been confirmed further by an X-ray analysis (Figure 1); selected interatomic distances and angles are listed in Table 2. The TiRu$_2$ triangle is capped by two μ_3-sulfido ligands, and the Ti−Ru(1) and Ru(1)−Ru(2) edges are bridged by a chloro ligand, which is almost coplanar with the three metal atoms. It is noteworthy that the Cl(2) atom is coordinated in a “semibridging” manner as substantiated by the unusually long Ru(1)−Cl(2) (2.563(2) Å) and the normal Ru(2)−Cl(2) (2.390(2) Å) distances. In contrast, the two capping sulfido ligands are located closer to the Ru(1) atom than to the Ru(2) atom: the Ru(1)−S distances (2.408 Å (mean)) are significantly shorter than the Ru(2)−S distances (2.513 Å (mean)).

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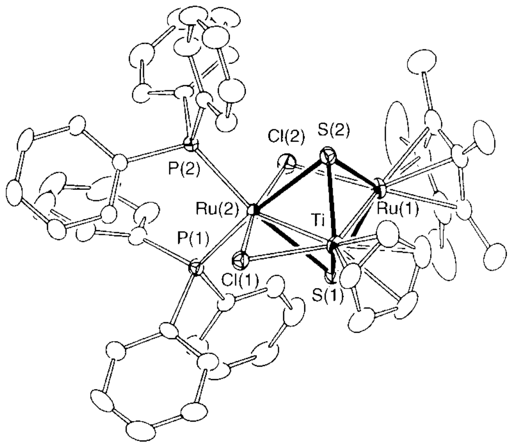


Figure 1. Structure of **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

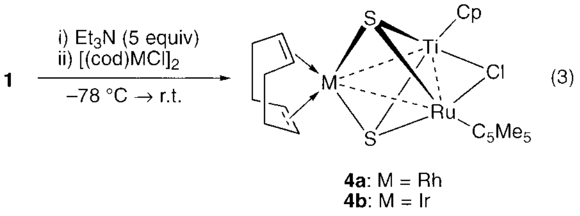
Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **3**

Ti−Ru(1)	3.032(1)	Ru(1)−Cl(2)	2.563(2)
Ti−Ru(2)	2.714(1)	Ru(2)−S(1)	2.521(2)
Ti−S(1)	2.266(2)	Ru(2)−S(2)	2.504(2)
Ti−S(2)	2.269(2)	Ru(2)−Cl(1)	2.432(2)
Ti−Cl(1)	2.357(2)	Ru(2)−Cl(2)	2.390(2)
Ru(1)−Ru(2)	3.188(2)	Ru(2)−P(1)	2.370(2)
Ru(1)−S(1)	2.408(2)	Ru(2)−P(2)	2.343(2)
Ru(1)−S(2)	2.408(2)		
Ru(1)−Ti−Ru(2)	67.12(3)	Ti−S(2)−Ru(2)	69.12(6)
Ti−S(1)−Ru(1)	80.83(7)	Ru(1)−S(2)−Ru(2)	80.91(6)
Ti−S(1)−Ru(2)	68.85(6)	Ti−Cl(1)−Ru(2)	69.04(5)
Ru(1)−S(1)−Ru(2)	80.56(6)	Ru(1)−Cl(2)−Ru(2)	80.03(6)
Ti−S(2)−Ru(1)	80.76(7)		

In the titanium−ruthenium heterobimetallic compounds reported so far, the Ti−Ru bond distances are put into two categories: one is found in complexes containing Ti−Ru bonds without bridging ligands (2.503(1)−2.663(1) Å)[30,31] and the other in cubane-type sulfido clusters synthesized by our group (2.904(2)−3.0158(8) Å).[21−23] The Ti−Ru(2) distance of 2.714(1) Å in the present $TiRu_2$ cluster **3** lies in the middle of these two categories, and the remarkably acute Ti−Cl(1)−Ru(2) and Ti−S−Ru(2) angles (69.0° (mean)) in **3** further support the presence of a Ti−Ru bond. On the other hand, the Ti−Ru(1) distance (3.032(1) Å) is much longer than the Ti−Ru(2) distance. However, it is only slightly longer than those of the latter category of Ti−Ru bond distances and still suggests the presence of some bonding interaction. In contrast to these Ti−Ru interactions, the Ru(1)−Ru(2) separation of 3.188(2) Å in **3** precludes any direct metal−metal bonding. The metal−metal bonding scheme is apparently inconsistent with the effective atomic number (EAN) rule, because the total electron count of **3** is 48 when the "semibridging" chloro ligand is treated as a bridging ligand. This can be accounted by the weak tendency of early transition metals to attain an $18e^-$ configuration. If the metal−metal interactions are neglected, the coordination geometry around the Ti and Ru(1) atoms is a three-legged piano-stool geometry, whereas that around the Ru(2) atom is distorted octahedral.

By virtue of the versatile coordination ability of sulfur, a number of triangular sulfido clusters containing two distinct metals have been synthesized by using terminal or bridging sulfido complexes[32−36] along with hydrosulfido,[13−18,37−39] disulfido,[40−43] and thiolato[44] complexes as building blocks. In the resultant MM'_2 heterobimetallic clusters, however, the ancillary ligands on the two M′ atoms are usually the same ones. Stepwise incorporation of M′ typified by eqs 1 and 2 enables the preparation of MM'_2 heterobimetallic clusters with two site-differentiated M′ centers.

Synthesis of TiRuM (M = Rh, Ir) Heterotrimetallic Clusters 4. According to the procedure for the synthesis of the $TiRu_2$ cluster **3**, the TiRuM heterotrimetallic clusters $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{M(cod)\}(\mu_3\text{-}S)_2(\mu_2\text{-}Cl)]$ (M = Rh (**4a**), Ir (**4b**)) were successfully obtained from the hydrosulfido-bridged titanium−ruthenium complex **1** and $[\{(cod)M\}_2(\mu_2\text{-}Cl)_2]$ with the aid of triethylamine (eq 3). As in the preparation of **3**,



treatment of **1** with triethylamine prior to addition of the group 9 metal complexes proved to be essential, because the reaction barely took place without triethylamine at room temperature. The ^1H NMR spectra of **4** indicate the presence of the Cp, C_5Me_5, and cod ligands in a ratio of 1:1:1, suggesting the TiRuM core composition of **4**.

The detailed structures of both **4a** and **4b** have been determined by X-ray crystallography (Figure 2); selected bond distances and angles are listed in Table 3. The structures of these two clusters are essentially identical. Thus, clusters **4** have a TiRuM (M = Rh, Ir) triangular core with two capping sulfido ligands. Furthermore, a semibridging Cl ligand attaches to the Ti−Ru edge with long Ru−Cl distances of 2.574(2) Å (in **4a**) and 2.558(2) Å (in **4b**); the Ti−Cl distances (**4a**, 2.344(2) Å; **4b**, 2.350(2) Å) are comparable to that in **3** (2.357(2) Å). The remarkably acute Ti−Cl−Ru angle (**4a**, 66.27(5)°; **4b**, 66.86(5)°) as well as the Ti−Ru distances (**4a**, 2.695(1) Å; **4b**, 2.710(2) Å) indicates the presence of a Ti−Ru bond. The Ti−Rh distance in **4a** (2.941(1) Å) falls in the range of those found in

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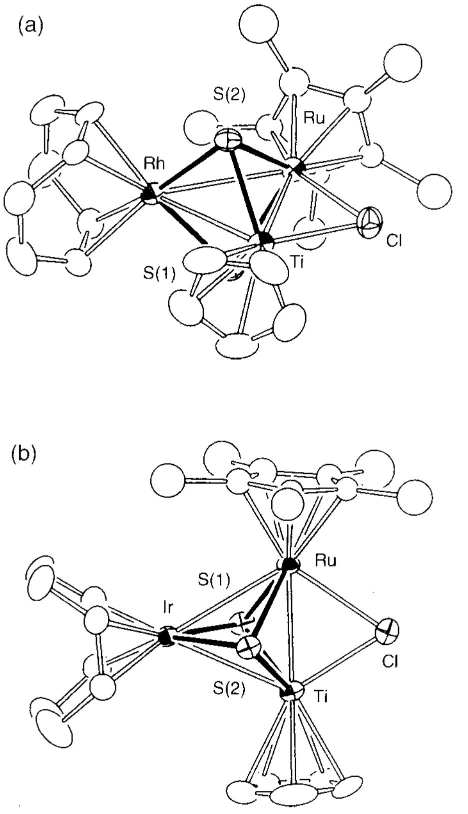


Figure 2. Structures of (a) **4a** and (b) **4b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and the minor component of the disordered C_5Me_5 groups are omitted for clarity.

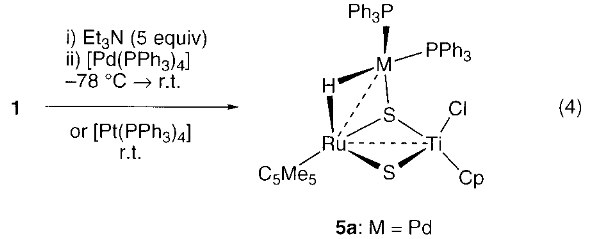
Table 3. Selected Bond Distances (Å) and Angles (deg) for **4a** and **4b**

	4a (M = Rh)	**4b** (M = Ir)
Ti−Ru	2.695(1)	2.710(2)
Ti−M	2.941(1)	2.878(1)
Ti−S(1)	2.275(2)	2.292(2)
Ti−S(2)	2.279(2)	2.283(2)
Ti−Cl	2.344(2)	2.350(2)
Ru−M	3.018(1)	2.9535(6)
Ru−S(1)	2.427(2)	2.445(2)
Ru−S(2)	2.444(2)	2.432(2)
Ru−Cl	2.574(2)	2.558(2)
M−S(1)	2.356(2)	2.347(2)
M−S(2)	2.355(2)	2.352(2)
Ru−Ti−M	64.59(3)	63.73(3)
Ti−Ru−M	61.66(3)	60.91(3)
Ti−M−Ru	53.75(3)	55.36(3)
Ti−S(1)−Ru	69.85(5)	69.69(7)
Ti−S(1)−M	78.84(6)	76.67(6)
Ru−S(1)−M	78.24(5)	76.06(6)
Ti−S(2)−Ru	69.48(6)	70.07(6)
Ti−S(2)−M	78.77(6)	76.75(6)
Ru−S(2)−M	77.93(6)	76.21(5)
Ti−Cl−Ru	66.27(5)	66.86(5)

related Ti−Rh sulfido clusters such as $[(CpTi)_2\{Rh(cod)\}_2(\mu_3\text{-}S)_4]$,[45] $[CpTi(\mu_3\text{-}S)_3\{Rh(tfbb)\}_3]$ (tfbb = tetrafluorobenzobarrelene),[46] and $[(CpTi)_2\{Rh(CO)\}_2\{Rh(CO)[P(OPh)_3]\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4]$ (2.8779(7)−3.056(1) Å).[47] Similarly, the Ti−Ir distance of 2.878(1) Å in **4b** is comparable to those found in $[CpTi(\mu_3\text{-}S)_3Ir_3(\mu_2\text{-}CO)(CO)_3\{P(OMe)_3\}_3]$ (2.815 Å (mean of the shorter distances)),[48] $[TiCl_2(\mu_2\text{-}S)_2Ir(PMe_3)(\eta^5\text{-}C_5Me_5)]$ (2.899(1) Å),[49] and $[CpTiCl(\mu_2\text{-}S)_2Ir(PMe_3)(\eta^5\text{-}C_5Me_5)]$ (2.989(2) Å),[49] in which the presence of an Ir−Ti dative bond is suggested. On the other hand, the Ru−Rh(Ir) distances of 3.018(1) and 2.9535(6) Å in **4** indicate that the interactions between these metal atoms are relatively weak, when these distances are compared with, for example, the Ru−Rh distances found in $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_2\text{-}H)(\mu_3\text{-}S)_2RhCl_2(PPh_3)]$ (2.773 Å (mean)).[14] This is partially because of the high-lying atomic p_z orbital perpendicular to the coordination plane of the Rh(Ir) atom.[50] We also note that the Ru−Ir distance in **4b** is still close to those in $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2(\mu_3\text{-}S)_2RuMe(dppe)][PF_6]$ (2.8695(8) and 2.978(1) Å; dppe = $Ph_2PCH_2CH_2PPh_2$).[18] As a consequence of the electron-deficient nature of titanium, clusters **4** have only 46 electrons.

With regard to a related reaction, the hydrosulfido-bridged homodinuclear complexes $[(\eta^5\text{-}C_5Me_5)MCl(\mu_2\text{-}SH)_2MCl(\eta^5\text{-}C_5Me_5)]$ (M = Rh, Ir) are known to react with $[\{(cod)Rh\}_2(\mu_2\text{-}Cl)_2]$ to afford the 48e$^-$ RhM_2 clusters $[\{(\eta^5\text{-}C_5Me_5)M\}_2(\mu_3\text{-}S)_2Rh(cod)]^+$ with three metal−metal bonds.[15] Unlike the formation of **4**, these reactions take place without addition of bases. Oro, Ciriano, and co-workers have recently prepared the Zr−Rh−Ir heterotrimetallic triangular cluster $[(Cp^{tt}{}_2Zr)\{Rh(cod)\}\{Ir(CO)_2\}(\mu_3\text{-}S)_2]$ (Cp^{tt} = $\eta^5\text{-}C_5H_3Bu^t{}_2\text{-}1,3$) by the salt-elimination reaction of the sulfido-bridged zirconium−iridium anion $[Cp^{tt}{}_2Zr(\mu_2\text{-}S)_2Ir(CO)_2]^-$ with $[\{(cod)Rh\}_2(\mu_2\text{-}Cl)_2]$.[39] This ZrRhIr cluster has a Rh−Ir bond, whereas there seems to be no significant interaction between the d^0 zirconium center and the d^8 late-transition-metal centers. The heterotrimetallic triangular cluster $[PPN]_2[CrMoW(\mu_3\text{-}S)(\mu_2\text{-}CO)_3(CO)_9]$ (PPN = $(Ph_3P)_2N^+$) has also been synthesized by a bridge-assisted nuclearity expansion from the hydrosulfido complex $[PPN][W(SH)(CO)_5]$.[51] In contrast to **4**, these clusters contain more than two metals that belong to the same group in the periodic table.

Synthesis and Structures of TiRuM (M = Pd, Pt) Heterotrimetallic Clusters 5. Successful isolation of clusters **3** and **4** encouraged us to apply the same synthetic procedure to group 10 metals. As expected, complex **1** reacted with $[Pd(PPh_3)_4]$ and triethylamine to afford the TiRuPd cluster $[(CpTiCl)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Pd(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ (**5a**), as shown in eq 4. Although the reaction of **1** with $[Pd(PPh_3)_4]$ alone also took place to give **5a**, addition of triethylamine made isolation of **5a** easier. On the other hand, the reaction of **1** with $[Pt(PPh_3)_4]$ was rather complicated. The reaction mixture was found



(4)

5a: M = Pd
5b: M = Pt

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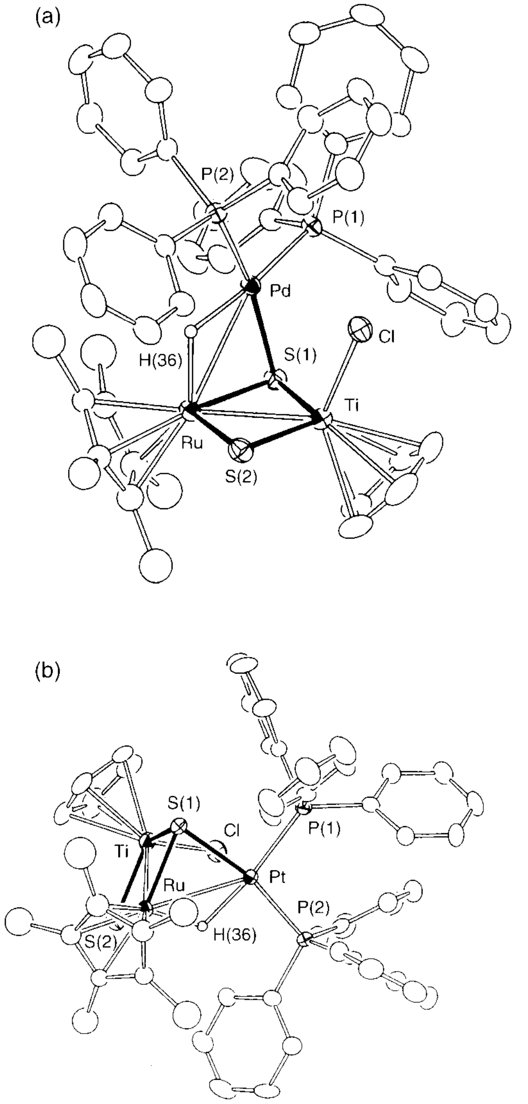

Figure 3. Structures of (a) **5a** and (b) **5b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms, except for the hydrido ligand, and the minor component of the disordered C_5Me_5 groups are omitted for clarity.

to contain the Ti_2Ru_2 cubane-type cluster **2** and *trans*-$[PtHCl(PPh_3)_2]$[52] along with the desired TiRuPt cluster, $[(CpTiCl)\{(\eta^5\text{-}C_5Me_5)Ru\}\{Pt(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ (**5b**). Fortunately, we succeeded in isolating **5b** by repeated recrystallization, although the yield was low. Addition of triethylamine did not improve the yield of **5b**.

The ^1H NMR spectra of **5** exhibit a hydrido resonance as a doublet of doublets, and in the case of the platinum cluster **5b**, the signal is further accompanied by ^{195}Pt satellites. The larger $^2J_{PH}$ values (**5a**, 114.7 Hz; **5b**, 119.6 Hz) are ascribed to the coupling with the phosphorus nucleus trans to the hydrido ligand, whereas the smaller values (**5a**, 4.9 Hz; **5b**, 14.6 Hz) are ascribed to that with the cis ligand. The inequivalency of the two phosphine ligands is also indicated by two mutually coupled signals in the $^{31}P\{^1H\}$ NMR spectra of **5**; Pt−P couplings with the $^1J_{PtP}$ values of 3659.9 and 3415.3 Hz are also observed for **5b**.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **5a** and **5b**

	5a (M = Pd)	**5b** (M = Pt)
Ti−Ru	2.821(1)	2.836(2)
Ti−M	3.270(1)	3.331(2)
Ti−S(1)	2.338(2)	2.355(3)
Ti−S(2)	2.210(2)	2.208(3)
Ti−Cl	2.349(2)	2.336(3)
Ru−M	2.8972(5)	2.9043(8)
Ru−S(1)	2.297(1)	2.324(2)
Ru−S(2)	2.356(2)	2.361(3)
Ru−H(36)	1.75	1.69
M−S(1)	2.344(1)	2.341(2)
M−P(1)	2.378(1)	2.324(2)
M−P(2)	2.329(1)	2.283(2)
M−H(36)	1.77	1.79
Ti−Ru−M	69.74(2)	70.93(4)
Ti−S(1)−Ru	74.98(4)	74.62(8)
Ti−S(1)−M	88.59(5)	90.34(9)
Ru−S(1)−M	77.25(4)	77.01(7)
Ti−S(2)−Ru	76.25(5)	76.65(9)

The structures of **5a** and **5b** determined by X-ray crystallography are depicted in Figure 3, and selected interatomic distances and angles are listed in Table 4. The structures of both clusters are closely related to each other. The Ti−Ru distances (**5a**, 2.821(1) Å; **5b**, 2.836(2) Å) are slightly longer than those found in **3** and **4** but still indicate the presence of a metal−metal bond. In each complex, a hydrido ligand, which has been found in the final difference Fourier map, bridges the Ru−Pd and Ru−Pt edge to form a three-center−two-electron bond (Ru−Pd, 2.8972(5) Å; Ru−Pt, 2.9043(8) Å). On the other hand, the long Ti−Pd and Ti−Pt distances (3.270(1) and 3.331(2) Å) suggest the absence of direct Ti−Pd(Pt) interactions. If these metal−metal interactions are neglected, the Ti and Ru center have three-legged piano-stool geometries, whereas the Pd and Pt centers lie in a square-planar environment.

The $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)$ framework found in **5** is unprecedented for clusters with M_3S_2 composition.[53] Indeed, the long Pd−S(2) and Pt−S(2) distances of 4.030(2) and 4.062(2) Å clearly distinguish the $TiRuPdS_2$ and $TiRuPtS_2$ cores in **5** from the typical $M_3(\mu_3\text{-}S)_2$ one. It is also to be noted that the Ti−(μ_2-S) distances (**5a**, 2.210(2) Å; **5b**, 2.208(3) Å) are significantly shorter than the Ti−(μ_3-S) distances (**5a**, 2.338(2) Å; **5b**, 2.355(3) Å) and are comparable to the Ti═S double-bond distances (2.111−2.217(1) Å).[54−57] In contrast, the Ru−(μ_2-S) distances (**5a**, 2.356(2) Å; **5b**, 2.361(3) Å) are slightly longer than the Ru−(μ_3-S) distances (**5a**, 2.297(1) Å; **5b**, 2.324(2) Å). The chloro ligand is bonded to the Ti atom as a terminal ligand with the Pd−Cl and Pt−Cl nonbonding contacts of 3.203(2) and 3.379(3) Å.

We have already demonstrated that the hydrosulfido-bridged diiridium complex $[(\eta^5\text{-}C_5Me_5)IrCl(\mu_2\text{-}SH)_2IrCl(\eta^5\text{-}C_5Me_5)]$ reacts with $[Pd(PPh_3)_4]$ to afford the Ir_2Pd cluster $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2(\mu_3\text{-}S)_2PdCl(PPh_3)]Cl$.[15] Interestingly, the corresponding reaction of the diruthenium complex $[(\eta^5\text{-}C_5Me_5)RuCl(\mu_2\text{-}SH)_2RuCl(\eta^5\text{-}C_5Me_5)]$ leads to the formation of the ruthenium−palladium cluster $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_3\text{-}S)_2\{Pd(PPh_3)\}_2(\mu_2\text{-}Cl)]Cl$ with a Ru_2Pd_2 composition.[58] In these reactions, including the formation of **5**, the sum of the formal oxidation number of

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the metals is increased by 2. If oxidation of the metal atoms does not take place as in eqs 2 and 3, it would be expected that $[(CpTi)\{(\eta^5\text{-}C_5Me_5)Ru\}\{M(PPh_3)_2\}(\mu_3\text{-}S)_2]$ (**6**) is formed. We thus attempted the dehydrochlorination of **5a** with strong bases such as $NaN(SiMe_3)_2$. Being consistent with the formation of **6** (M = Pd), the ^1H NMR spectrum of the reaction mixture exhibited new singlets at 6.18 and 1.49 ppm in an intensity ratio of 5:15 along with the signals ascribed to the Ti_2Ru_2 cubane-type cluster **2**. However, further characterization of this new species has been unsuccessful so far.

Concluding Remarks

We have systematically synthesized heterometallic triangular sulfido clusters **3**−**5** bearing $TiRu_2$ and TiRuM (M = Rh, Ir, Pd, Pt) cores by stepwise accumulation of two distinct metal fragments onto the hydrosulfido complex $[Cp_2Ti(SH)_2]$. These clusters have been added to the cluster library as a novel class of compounds. It is of special note that, to the best of our knowledge, clusters **4** and **5** represent the first examples of heterotrimetallic triangular clusters containing titanium. All of the clusters synthesized in the present study have a $TiRuMS_2$ core composition in common, along with a chloro ligand bound to the Ti atom. Owing to the different nature of the metals involved, however, the $TiRuMS_2$ cores are significantly deformed from a symmetrical M_3S_2 trigonal bipyramid, depending notably upon the incoming metal M. Such deformation leads to the structural characteristics exemplified by the unprecedented $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)$ core in **5** and the “semibridging” chloro ligand in **3** and **4**. In addition, clusters **3**−**5** do not obey the EAN rule because of the electron-deficient nature of titanium.

It is also to be emphasized that clusters **3**−**5** contain more than two very different metal centers with labile chloro, organophosphine, and olefinic coligands in close proximity. We believe cooperative reactivities are elicited from these early−late heterometallic centers.[59] Further investigation will be directed toward this line.

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Supporting Information Available: X-ray crystallographic files in CIF format for **3**, **4a**, **4b**, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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