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Synthesis of a New Family of Heteronuclear Thiolate Iron Complexes that Contain Isocyanide Ligands

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Treatment of complex $[\mathrm{Cp^{\star}Fe}(\mu\text{-SEt})_3\mathrm{FeCp^{\star}}]$ (**1**; $\mathrm{Cp^{\star}}$ = pentamethylcyclopentadienyl) with isocyanides CNR affords the mononuclear complexes $[\mathrm{Cp^{\star}FeSEt(CNR)_2}]$ (**2a**, R = *t*Bu; **2b**, R = Ph; **2c**, R = Cy; **2d**, R = Bn) in moderate yield. The heterobinuclear complexes $[\mathrm{Cp^{\star}FeCNR}(\mu\text{-CNR})(\mu\text{-SEt})\mathrm{PdCl(PPh_3)}][\mathrm{PF_6}]$ (**3a**, R = *t*Bu; **3b**, R = Ph; **3c**, R = Cy; **3d**, R = Bn), $[\mathrm{Cp^{\star}Fe(CN}t\mathrm{Bu)_2}(\mu\text{-SEt})\mathrm{NiCl(PPh_3)}][\mathrm{PF_6}]$ (**4**), and heterotrinuclear complexes $[\{\mathrm{Cp^{\star}Fe(CN}t\mathrm{Bu)_2}(\mu\text{-SEt})\}_2\mathrm{M}][\mathrm{PF_6}]$ (**5**, M = Au; **6**, M = Ag; **7**, M = Cu) have been prepared by the reaction of **2** with complexes $[\mathrm{PdCl_2(PPh_3)_2}]$, $[\mathrm{NiCl_2(PPh_3)_2}]$, and $[\mathrm{(Ph_3P)M}][\mathrm{X}]$ (X = $\mathrm{PF_6}$ or OTf, OTf = $\mathrm{OSO_2CF_3}$), respectively. These complexes have been spectroscopically and crystallographically characterized.

Introduction

Heteronuclear complexes are of broad interest due to the differences these systems have in their bonding and reactivity versus homonuclear species.[1] With two or more disparate metal centers in a single molecule, the potential exists for cooperative behavior that can improve the selectivity and efficiency of catalyzation and can promote reactions that are not possible using a single metal center.[2] Iron–sulfur complexes have received increasing attention on account of their unusual structures and occurrence in biological metalloproteins including nitrogenase, hydrogenase, and ferredoxins.[3] Acting as the active sites in numerous proteins in various organisms, they usually serve as electron-transport functionalities and complete biological reactions through cooperative actions of many metal centers in the form of clusters.[4] The chemistry of heteronuclear iron complexes with group 10 (Ni, Pd, and Pt)[5] and 11 (Au, Ag, and Cu)[6] metals have been extensively studied for the catalytic activity and application in material science, and these complexes are mainly stabilized by bridging neutral ligands (such as CO and phosphane ligands) or sulfide ligands. However, the thiolate-bridged heterobinuclear or heterotrinuclear complexes, especially those that contain Au and Ag atoms, have rarely been investigated.

It is commonly known that isocyanide molecules can be regarded as ligands that have a lone pair of electrons at the carbon atom like that in carbenes. Homobinuclear complexes with isocyanide have recently been studied a great deal and these complexes show some unique properties.[7] In our previous work, we reported thiolate-bridged diiron complexes that contain isocyanide ligands with excellent properties for the activation of C–Cl of some chlorohydrocarbons,[8] whereas the heterobinuclear isocyanide-bridged complexes that contain iron atoms have scarcely been reported, and the only example is $[\mathrm{(CO)_3Fe}(\mu\text{-CNR})(\mu\text{-dppm})\mathrm{Pt(PPh_3)}]$ (R = 2,6-xylyl or *o*-anisyl).[9] Additionally, complexes that contain noble metals can be used as catalysts in various kinds of organic transformations such as C–C bond-forming reactions.[10] These findings prompted us to synthesize new heteronuclear thiolate iron complexes with noble metals that contain isocyanide ligands, which might show some unique properties. Herein we report our preliminary results on the preparation of heterobinuclear Fe–SEt–M (M = Pd or Ni) complexes and heterotrinuclear Fe–SEt–M–SEt–Fe (M = Au, Ag, or Cu) complexes and their spectroscopic and crystallographic characterizations.

Results and Discussion

Synthesis and Characterization of $[\mathrm{Cp^*FeSEt(CNR)_2}]$ (2a, R = *t*Bu; 2b, R = Ph; 2c, R = Cy; 2d, R = Bn)

Treatment of the binuclear complex $[\mathrm{Cp^*Fe}(\mu\text{-SEt})_3\mathrm{FeCp^*}]$ (**1**; Cp* = pentamethylcyclopentadienyl) with CNR (5 equiv.) in THF at room temperature for 12 h afforded mononuclear complex $[\mathrm{Cp^*FeSEt(CNR)_2}]$ (**2**) as a brown-red solid in moderate yield (Scheme 1). Several isocyanides with different R substituents were used, and all of the resulting complexes were found to be air-sensitive. Stability was found to decrease in the sequence Ph > *t*Bu > Cy > Bn. The ^{1}H NMR spectra of **2** in $\mathrm{C_6D_6}$ show one broad signal at δ = 1.78, 1.79, 1.84, and 1.73 ppm, which is attributed to the Cp* protons for **2a**, **2b**, **2c**, and **2d**, respectively.

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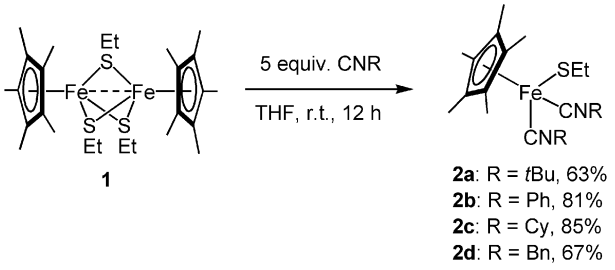
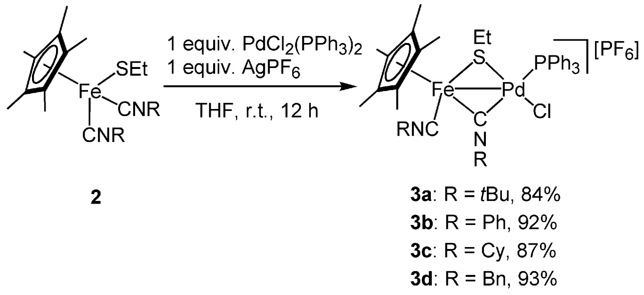
The IR bands at 2099, 2058, and 1990 cm^{-1} (**2a**), 2089, 2039, and 2001 cm^{-1} (**2b**), 2090, 2043, and 1998 cm^{-1} (**2c**), and 2103, 2054, and 2004 cm^{-1} (**2d**) are indicative of the terminal end-on coordination mode of the CNR ligand.[8] The EI-MS mass spectra give the parent peak at *m*/*z* = 418.2104 for **2a**, 458.1488 for **2b**, 470.2421 for **2c**, and 486.1797 for **2d**, and the successive loss of two isocyanide ligands before further fragmentation.



Scheme 1. Synthesis of complexes **2a**, **2b**, **2c**, and **2d**.

Synthesis and Characterization of [Cp*FeCNR(μ-CNR)(μ-SEt)PdCl(PPh$_3$)][PF$_6$] (3a, R = *t*Bu; 3b, R = Ph; 3c, R = Cy; 3d, R = Bn)

We chose complex **2** as the starting material to investigate its reactivity in the formation of heterometal complexes. As outlined in Scheme 2, treatment of [Cp*FeSEt(CNR)$_2$] (**2**) with [PdCl$_2$(PPh$_3$)$_2$] (1 equiv.) and AgPF$_6$ in THF at room temperature affords complexes [Cp*FeCNR(μ-CNR)(μ-SEt)PdCl(PPh$_3$)][PF$_6$] (**3a**, R = *t*Bu; **3b**, R = Ph; **3c**, R = Cy; **3d**, R = Bn) in 84, 92, 87, and 93% yields (based on **2**) as a dark violet-red microcrystalline solid, respectively. Compounds **3a**–**3d** displayed excellent solubility in acetonitrile, acetone, methonal, and tetrahydrofuran, and are sparingly soluble in ether or hexane.



Scheme 2. Synthesis of complexes **3a**, **3b**, **3c**, and **3d**.

The ^{1}H NMR spectra of **3a**, **3b**, **3c**, and **3d** in [D$_6$]acetone show a broad singlet at δ = 1.95, 2.12, 1.96, and 1.89 ppm, which is attributed to the Cp* protons. The signals for CH$_2$ protons of μ-SEt in **3a** and **3c** exhibit a quartet at δ = 1.53 and 0.88 ppm, respectively, whereas two multiplets appear at δ = 1.82 and 1.61 ppm in **3b** and at δ = 1.52 and 1.36 ppm in **3d**. Except for the signal of the PF$_6$ anion, the ^{31}P{^{1}H} NMR spectra of **3a**, **3b**, **3c**, and **3d** exhibit one signal at δ = 30.2, 31.0, 29.7, and 29.4 ppm, respectively, due to the PPh$_3$ ligand. The structures of **3a**, **3b**, **3c**, and **3d** are unambiguously characterized by single-crystal X-ray diffraction analysis, and their spectral features are fully consistent with their crystal structures. ORTEP drawings of the **3a** and **3b** cations are shown in Figure 1 and Figure 2 (for **3c** and **3d**, see Figures S1 and S2 in the Supporting Information). Selected bond lengths and angles of **3a**–**3d** are listed in Table 1.

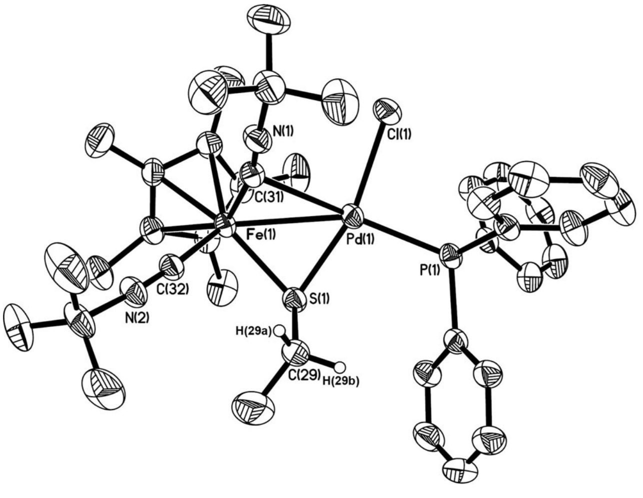


Figure 1. ORTEP (ellipsoids at 30% probability) drawing of the cation of **3a**. All hydrogen atoms except for the hydrogen atoms at C(29) are omitted for clarity.

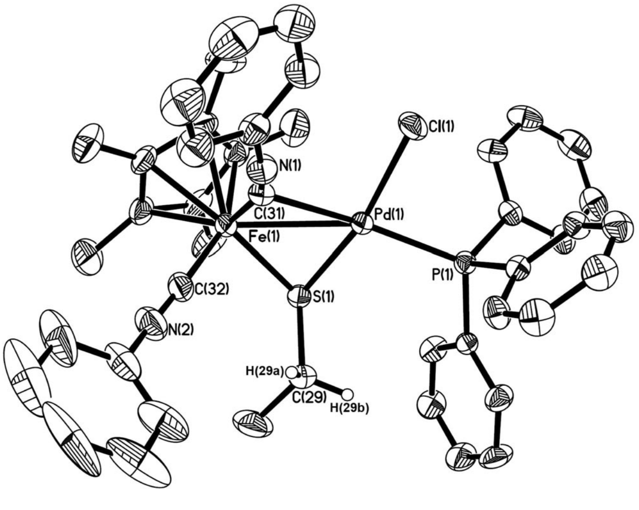


Figure 2. ORTEP (ellipsoids at 30% probability) drawing of the cation of **3b**. All hydrogen atoms except for the hydrogen atoms at C(29) are omitted for clarity.

From the molecular structures of the cation of **3** we can see that two transition-metal fragments [Cp*Fe(CNR)] and [PdCl(PPh$_3$)] are bridged by an isocyanide ligand and a thiolate ligand. To the best of our knowledge, complexes **3** are the first examples of a bridging isocyanide ligand between iron and palladium atoms. Ignoring the metal–metal bond, the geometry at the iron center is that of a three-legged piano stool; it contains one terminal and one bridging isocyanide group, as commonly observed in homonuclear thiolate-bridged diiron complexes.[8] The Fe(1)–Pd(1)

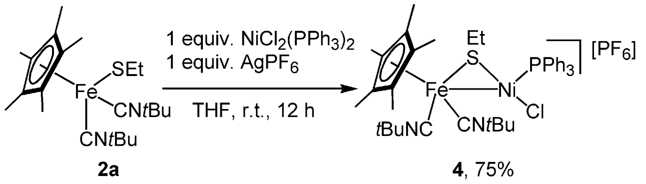
Table 1. Selected bond lengths [Å] and bond angles [°] of complexes **3a**–**3d**.

3a			
Fe(1)–Pd(1)	2.7409(7)	C(31)–N(1)	1.153(6)
Fe(1)–S(1)	2.2099(12)	C(32)–N(2)	1.139(5)
Fe(1)–C(31)	1.859(6)	Fe(1)–S(1)–Pd(1)	76.49(4)
Fe(1)–C(32)	1.858(4)	Fe(1)–C(31)–Pd(1)	74.86(16)
Pd(1)–S(1)	2.2179(12)	S(1)–Fe(1)–C(31)	102.75(13)
Pd(1)–P(1)	2.2753(11)	S(1)–Fe(1)–C(32)	93.58(13)
Pd(1)–C(31)	2.558(4)	S(1)–Pd(1)–C(31)	83.38(12)
3b			
Fe(1)–Pd(1)	2.7180(9)	C(31)–N(1)	1.166(5)
Fe(1)–S(1)	2.2115(13)	C(32)–N(2)	1.169(6)
Fe(1)–C(31)	1.861(5)	Fe(1)–S(1)–Pd(1)	75.34(4)
Fe(1)–C(32)	1.818(5)	Fe(1)–C(31)–Pd(1)	77.72(15)
Pd(1)–S(1)	2.2361(11)	S(1)–Fe(1)–C(31)	105.21(13)
Pd(1)–P(1)	2.2749(11)	S(1)–Fe(1)–C(32)	95.03(14)
Pd(1)–C(31)	2.416(4)	S(1)–Pd(1)–C(31)	88.29(11)
3c			
Fe(1)–Pd(1)	2.7139(11)	C(31)–N(1)	1.146(4)
Fe(1)–S(1)	2.1999(10)	C(32)–N(2)	1.150(4)
Fe(1)–C(31)	1.857(4)	Fe(1)–S(1)–Pd(1)	75.58(4)
Fe(1)–C(32)	1.848(4)	Fe(1)–C(31)–Pd(1)	74.28(12)
Pd(1)–S(1)	2.2287(9)	S(1)–Fe(1)–C(31)	104.02(11)
Pd(1)–P(1)	2.2736(11)	S(1)–Fe(1)–C(32)	93.77(11)
Pd(1)–C(31)	2.545(3)	S(1)–Pd(1)–C(31)	84.05(8)
3d			
Fe(1)–Pd(1)	2.7368(10)	C(31)–N(1)	1.155(5)
Fe(1)–S(1)	2.2169(13)	C(32)–N(2)	1.151(5)
Fe(1)–C(31)	1.870(4)	Fe(1)–S(1)–Pd(1)	75.92(4)
Fe(1)–C(32)	1.852(4)	Fe(1)–C(31)–Pd(1)	78.26(15)
Pd(1)–S(1)	2.2323(11)	S(1)–Fe(1)–C(31)	102.13(12)
Pd(1)–P(1)	2.2650(10)	S(1)–Fe(1)–C(32)	93.50(12)
Pd(1)–C(31)	2.415(4)	S(1)–Pd(1)–C(31)	86.48(10)

bond length [2.7139(7)–2.7409(11) Å] of **3a**–**3d** falls in the 2.5–2.8 Å range of those reported for heterobinuclear complexes that contain Fe–Pd bonds.[11] Completely different from the heterobinuclear Fe–Pt complexes [(CO)$_3$Fe(μ-CNR)(μ-dppm)Pt(PPh$_3$)] with a bridging isocyanide ligand that has a nearly equal distance to Fe and Pt atoms,[9] the bridging isocyanide ligand in **3a**–**3d** is clearly leaning to the iron center, and the Fe(1)–C(31) [1.859(6)–1.870(4) Å] bond lengths of **3a**–**3d** are moderately shorter by 0.55–0.70 Å than those of Pd(1)–C(31) [2.415(4)–2.558(4) Å]. In complexes **3b**–**3d**, the distance between Fe(1) and C(31) of the bridging isocyanide ligand is apparently longer than that between Fe(1) and C(32) of the terminal isocyanide ligand, whereas the corresponding Fe(1)–C(31) and Fe(1)–C(32) bond lengths in **3a** are nearly equal. The Fe(1)Pd(1)C(31)S(1) rings of **3a**–**3d** are substantially puckered with a dihedral angle of 133.6, 144.5, 134.5, and 139.3°, respectively. The Pd(1)–P(1) bond lengths [2.2650(10)–2.2753(11) Å] are shorter than those found in the precursor *trans*-[PdCl$_2$(PPh$_3$)$_2$] [2.337(1) Å].[12]

Synthesis and Characterization of [Cp*Fe(CN*t*Bu)$_2$(μ-SEt)NiCl(PPh$_3$)][PF$_6$] (4)

Encouraged by the successful syntheses of complexes **3**, we applied the synthetic method to other heteronuclear complexes with Ni metal. Using complex [NiCl$_2$(PPh$_3$)$_2$] as the substrate, we were able to achieve another new Fe–Ni heterobinuclear complex. Complex **2a** reacts readily with [NiCl$_2$(PPh$_3$)$_2$] (1 equiv.) and AgPF$_6$ in THF at room temperature to give complex [Cp*Fe(CN*t*Bu)$_2$(μ-SEt)NiCl(PPh$_3$)][PF$_6$] (**4**) in 75% yield (based on **2a**) as a black-brown microcrystalline solid (Scheme 3). When the above reaction is performed respectively with complexes **2b**, **2c**, or **2d** instead of **2a**, we can get similar structural products with different isocyanide ligands.



Scheme 3. Synthesis of complex **4**.

The ^{1}H NMR spectrum of **4** in CD$_3$CN displays one broad signal at δ = 2.59 ppm on account of the Cp* protons. Two broad signals at δ = 1.53 and 1.48 ppm are attributed to the two CN*t*Bu ligand protons. Except for the signal of the PF$_6$ anion, the ^{31}P{^{1}H} NMR spectrum of **4** shows one signal at δ = –5.9 ppm due to the PPh$_3$ ligand. The phosphane signal of PPh$_3$ is shifted by about 36 ppm to a higher field than that of **3a**. In addition, the IR bands at 2157 and 2132 cm^{-1} offer clear evidence of the terminal end-on coordination mode of the CN*t*Bu ligand. The structural features of **4** were confirmed by single-crystal X-ray diffraction analysis; the ORTEP drawing of the cation of **4** is shown in Figure 3. Selected bond lengths and angles of **4** are listed in Table 2.

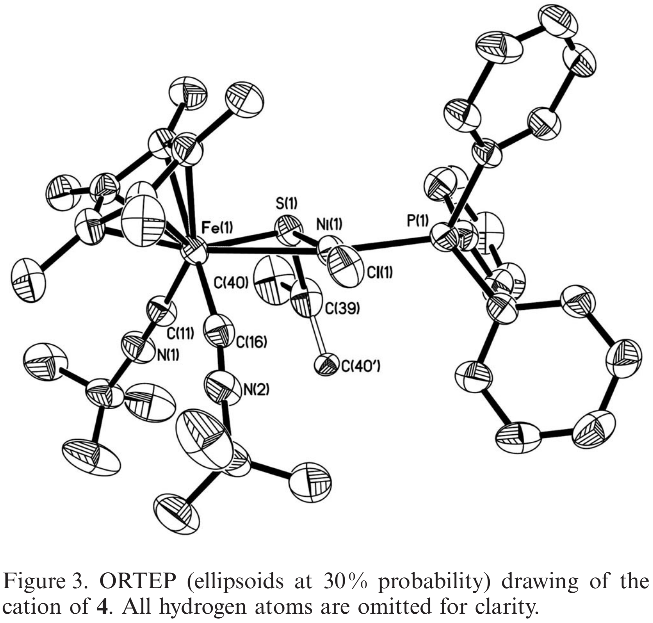


Figure 3. ORTEP (ellipsoids at 30% probability) drawing of the cation of **4**. All hydrogen atoms are omitted for clarity.

Compared to the molecular structures of **3a**–**3d**, with one thiolate ligand and one isocyanide ligand bridging the two metal centers Fe and Pd, the structure of the cation of **4**

Table 2. Selected bond lengths [Å] and bond angles [°] of **4**.

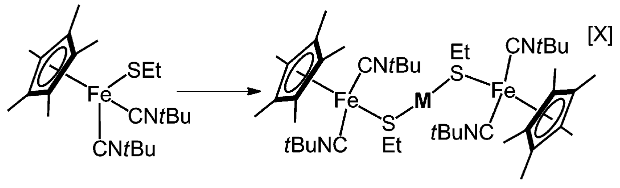
Fe(1)–Ni(1)	2.6734(13)	Fe(1)–S(1)	2.1989(17)
Fe(1)–C(11)	1.851(6)	Fe(1)–C(16)	1.851(6)
Ni(1)–S(1)	2.0952(17)	Ni(1)–P(1)	2.1910(17)
Ni(1)–Cl(1)	2.1926(18)	C(11)–N(1)	1.150(6)
C(16)–N(2)	1.157(7)	Fe(1)–S(1)–Ni(1)	76.97(6)
S(1)–Fe(1)–C(11)	93.29(18)	S(1)–Fe(1)–C(16)	102.23(19)
S(1)–Ni(1)–P(1)	100.97(6)	P(1)–Ni(1)–Cl(1)	95.44(6)

shows only one bridging thiolate ligand between the Fe and Ni atoms, and the other two isocyanide ligands are both terminally coordinated to the Fe center. The Ni atom is three-coordinate instead of four-coordinate as found in the precursor. The rigid pyramidalization of the sulfur atom results in the two nonequivalent CN*t*Bu ligands, which was also confirmed by ^{1}H NMR spectroscopy. The Fe(1)–Ni(1) bond length [2.6734(13) Å] is within the range (2.5–2.7 Å) of those for heterobinuclear complexes that contain Fe–Ni bonds.[13] The Ni(1)–P(1) bond length [2.1910(17) Å] is shorter than that in mononuclear complex *trans*-[NiCl$_2$(PPh$_3$)$_2$] [2.2439(5) Å].[14]

Synthesis and Characterization of [{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$M][PF$_6$] (5, M = Au; 6, M = Ag; 7, M = Cu)

The successful synthesis of complexes **3** and **4** prompted us to expand our synthetic approach to more challenging systems that contain group 11 metals (Au, Ag, and Cu) as the heterometals. To our surprise, we obtained three new heterotrinuclear iron complexes that contained Au, Ag, and Cu atoms. For example, treatment of **2a** with (Ph$_3$P)AuPF$_6$ (0.5 equiv.) in THF at room temperature produced complex [{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$Au][PF$_6$] (**5**) in moderate yield as dark brown-red crystals (Scheme 4). The reaction did not proceed at low temperature (from –78 to 0 °C). When **2a** was treated with (Ph$_3$P)AuPF$_6$ in a higher ratio of 6:1, we still obtained **5** together with the unreacted **2a**. In the same way, by using AgOTf or (Ph$_3$P)AgOTf and [CuPF$_6$-(MeCN)$_4$] or (Ph$_3$P)CuPF$_6$ as the substrate, we were able to get complexes [{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$Ag][OTf] (**6**) and [{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$Cu][PF$_6$] (**7**) in high yield. In addition, analogous products could be achieved with different isocyanide ligands when the starting material **2a** was replaced by **2b**, **2c**, or **2d**.

The ^{1}H NMR spectra of **5**, **6**, and **7** in CD$_3$CN individually show a broad singlet at δ = 1.64, 1.60, and 1.61 ppm attributed to two equivalent Cp* protons and one broad signal at δ = 1.51, 1.49, and 1.48 ppm on account of four equivalent CN*t*Bu ligand protons. The IR spectrum of **5**, **6**, and **7** (KBr) displays a strong band at 2050–2125 cm^{-1} on account of N≡C stretching of the terminal CN*t*Bu ligands. Compared with that of **2a**, the $\tilde{\nu}_{N\equiv C}$ bands of **5**, **6**, and **7** shift to higher wavenumbers.



2a

5: M = Au, X = PF$_6$
6: M = Ag, X = OTf
7: M = Cu, X = PF$_6$

Scheme 4. Synthesis of complexes **5**, **6**, and **7**. Reaction reagents and conditions: THF, room temp., 12 h; **5**: (Ph$_3$P)AuCl (0.5 equiv.) and AgPF$_6$ (0.5 equiv.), 52%; **6** (method A): AgOTf (0.5 equiv.), 81%; (method B): (Ph$_3$P)AgOTf (0.5 equiv.), 41%; **7** (method A): (Ph$_3$P)CuCl (0.5 equiv.) and AgPF$_6$ (0.5 equiv.), 74%; (method B): [CuPF$_6$(MeCN)$_4$] (0.5 equiv.), 86%.

The molecular structures of complexes **5**, **6**, and **7** have been determined by single-crystal diffraction analyses and are shown in Figures 4, 5, and 6. Significant bond parameters of **5**, **6**, and **7** are collectively given in Table 3. The oxidation states of all the metal atoms in the precursor compounds are retained in the products. The molecular structures of **5**, **6**, and **7** are analogous except for the central metal. For instance, the structure of **5** possesses a center of inversion at the central metal center, which is coordinated to two S donor atoms with a linear arrangement. The Cp* rings are oriented on opposite sides of the S–Au–S line. In the structures of **5**, **6**, and **7**, there is no Fe–M metal–metal bond (M = Au, Ag, or Cu). Thus, the flexible Fe(1)–S(1) bond and C_2 symmetry of the molecule result in the same chemical environment of the four CN*t*Bu ligands, which is consistent with their ^{1}H NMR spectra that show only one signal for the four equivalent CN*t*Bu ligands. The Fe(1)–S(1) bond length [2.2883(19)–2.3016(11) Å] of **5**, **6**, and **7** is slightly longer than that of diiron complexes **1** (average:

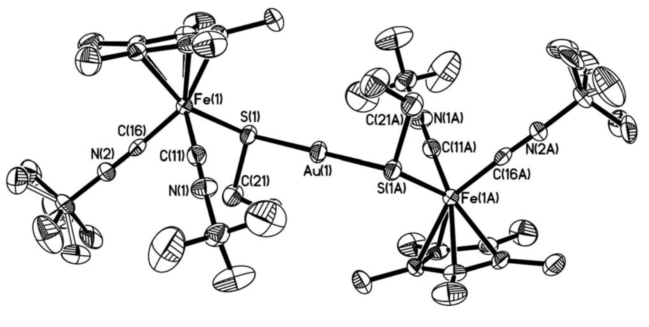


Figure 4. ORTEP (ellipsoids at 30% probability) drawing of the cation of **5**. All hydrgen atoms are omitted for clarity.

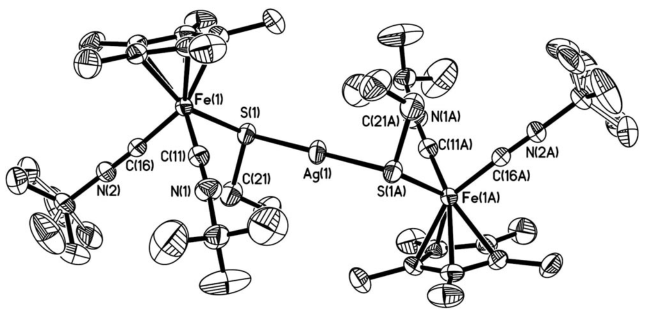


Figure 5. ORTEP (ellipsoids at 30% probability) drawing of the cation of **6**. All hydrogen atoms are omitted for clarity.

2.2638 Å), [Cp*FeSEt(μ-SEt)$_2$FeCN*t*BuCp*] (average: 2.2615 Å), and [Cl$_2$Fe(μ-SEt)$_2$FeCN*t*BuCp*] (average: 2.2567 Å).[8]

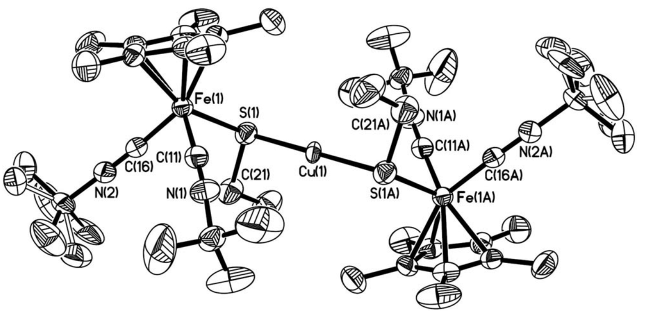


Figure 6. ORTEP (ellipsoids at 30% probability) drawing of the cation of **7**. All hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths [Å] and bond angles [°] of **5**, **6**, and **7**.

	5	6	7
Fe(1)–S(1)	2.2950(17)	2.3016(11)	2.2883(19)
Fe(1)–C(11)	1.834(7)	1.828(3)	1.786(6)
Fe(1)–C(16)	1.829(7)	1.824(3)	1.812(6)
M(1)–S(1)	2.3086(17)	2.3842(12)	2.260(2)
C(11)–N(1)	1.148(8)	1.161(4)	1.158(7)
C(16)–N(2)	1.147(8)	1.154(4)	1.180(7)
S(1)–M(1)–S(1)$^{\#1}$	180.00(2)	180.00(4)	180.00(8)
Fe(1)–S(1)–M(1)	108.70(6)	106.25(4)	106.48(7)
C(21)–S(1)–M(1)	102.3(2)	101.74(12)	102.8(2)
C(11)–Fe(1)–C(16)	89.2(3)	89.79(13)	89.8(2)
S(1)–Fe(1)–C(11)	91.7(2)	91.45(10)	91.90(19)
S(1)–Fe(1)–C(16)	95.12(18)	95.13(10)	95.04(17)

Conclusion

In summary, we have successfully synthesized four heterobinuclear complexes that contain the Pd atom, [Cp*FeCNR(μ-CNR)(μ-SEt)PdCl(PPh$_3$)][PF$_6$] (**3a**, R = *t*Bu; **3b**, R = Ph; **3c**, R = Cy; **3d**, R = Bn), one heterobinuclear Fe–Ni complex, [Cp*Fe(CN*t*Bu)$_2$(μ-SEt)NiCl(PPh$_3$)][PF$_6$] (**4**), and three heterotrinuclear complexes that contain Au, Ag, and Cu atoms, [{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$M][PF$_6$] (**5**, M = Au; **6**, M = Ag; **7**, M = Cu). It is noteworthy that this is the first time that heterobinuclear Fe–Pd complexes with bridging isocyanide and thiolate-linked heterotrinuclear Fe–SEt–M–SEt–Fe (M = Au and Ag) complexes have been reported. Such complexes with Cp* ligands and heterometals may show some remarkable properties in catalytic transformation and material science. Further investigations toward the synthesis of complexes with other heterometals are now in progress.

Experimental Section

General: All manipulations were routinely carried out under an argon atmosphere, using standard Schlenk-line techniques. All solvents were dried and distilled from an appropriate drying agent under argon. [PdCl$_2$(PPh$_3$)$_2$], [NiCl$_2$(PPh$_3$)$_2$], [CuPF$_6$(MeCN)$_4$], and AgPF$_6$ (or AgOTf) were available commercially and used without further purification. The reagents CN*t*Bu, CNPh, CNCy, and CNBn were purchased from Aldrich. The starting material [Cp*Fe(μ-SEt)$_3$FeCp*] (**1**),[8] (Ph$_3$P)CuCl,[15] (Ph$_3$P)AgOTf,[16] and (Ph$_3$P)AuCl[17] were prepared according to the literature methods.

The ^{1}H and ^{31}P NMR spectra were recorded with a Bruker 400 Ultra Shield™ spectrometer. Chemical shifts are reported in ppm externally referenced to SiMe$_4$ for ^{1}H and 85% H$_3$PO$_4$ for ^{31}P nuclei. IR spectra were recorded with a JASCO FTIR 430 spectrophotometer. HRMS (EI) spectra determinations were made with a GCT-MS instrument (Micromass, England). ESI-MS spectra determinations were made with a Micromass Q-Tof (Micromass, Wythenshawe, UK) mass spectrometer. Elemental analyses were performed with a Vario EL analyzer.

[Cp*FeSEt(CN*t*Bu)$_2$] (2a): CN*t*Bu (145 mg, 1.747 mmol) was added to a solution of **1** (190 mg, 0.336 mmol) in THF (10 mL). After being stirred at room temperature for 12 h, the resulting black-brown solution was evaporated to dryness in vacuo. The crude product was purified by column chromatography on alumina using Et$_2$O/hexane (1:2) as eluent to give **2a** as a dark red solid (175 mg, 0.419 mmol, 63%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 2.46 (q, J = 7.2 Hz, 2 H, CH_2), 1.78 (br. s, 15 H, Cp*-CH_3), 1.67 (t, J = 7.2 Hz, 3 H, CH_3), 1.19 (s, 18 H, *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2971 (w), 2910 (w), 2860 (vw), 2099 (vs), 2058 (vs), 1990 (vs), 1454 (m), 1366 (m), 1229 (m), 1211 (w), 1026 (w), 882 (w), 744 (m), 558 (m), 527 (m), 464 (w) cm^{-1}. HRMS (EI): calcd. for [M]$^+$ 418.2105; found 418.2104. C$_{22}$H$_{38}$FeN$_2$S (418.46): calcd. C 63.14, H 9.15, N 6.69; found C 63.15, H 9.17, N 6.70.

[Cp*FeSEt(CNPh)$_2$] (2b): The reaction was carried out analogously to the procedure described for **2a** by treatment of **1** (606 mg, 1.073 mmol) with CNPh (560 mg, 5.437 mmol). After the purification by column chromatography on alumina, **2b** (791 mg, 1.727 mmol, 81%) was obtained as a dark red solid. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.18–6.74 (m, 10 H, *Ph*), 2.66 (q, J = 8.0 Hz, 2 H, CH_2), 1.79 (br. s, 15 H, Cp*-CH_3), 1.65 (t, J = 8.0 Hz, 3 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2957 (w), 2904 (w), 2089 (vs), 2039 (vs), 2001 (vs), 1591 (m), 1488 (m), 1454 (w), 1375 (w), 1262 (vw), 1070 (w), 1024 (w), 803 (w), 750 (m), 684 (m), 569 (m), 534 (w), 487 (w) cm^{-1}. HRMS (EI): calcd. for [M]$^+$ 458.1479; found 458.1488. C$_{26}$H$_{30}$FeN$_2$S (458.44): calcd. C 68.12, H 6.60, N 6.11; found C 68.14, H 6.63, N 6.12.

[Cp*FeSEt(CNCy)$_2$] (2c): The reaction was carried out analogously to the procedures described for **2a** by treatment of **1** (160 mg, 0.283 mmol) with CNCy (160 mg, 1.468 mmol). After the purification by column chromatography on alumina, **2c** (225 mg, 0.479 mmol, 85%) was obtained as a dark red solid. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 2.51 (q, J = 7.2 Hz, 2 H, CH_2), 1.84 (br. s, 15 H, Cp*-CH_3), 1.71 (t, J = 7.2 Hz, 3 H, CH_3), 1.69–0.95 (m, 22 H, *cyclo*-C$_6H_{11}$) ppm. IR (KBr): $\tilde{\nu}$ = 2935 (w), 2855 (w), 2090 (vs), 2043 (vs), 1998 (vs), 1450 (m), 1362 (m), 1320 (m), 1261 (m), 1095 (m), 1025 (m), 891 (w), 863 (w), 801 (m), 659 (m), 582 (w), 531 (w), 494 (vw) cm^{-1}. HRMS (EI): calcd. for [M]$^+$ 470.2418; found 470.2424. C$_{26}$H$_{42}$FeN$_2$S (470.54): calcd. C 66.37, H 9.00, N 5.95; found C 66.40, H 9.03, N 5.96.

[Cp*FeSEt(CNBn)$_2$] (2d): The reaction was carried out analogously to the procedures described for **2a** by treatment of **1** (328 mg, 0.581 mmol) with CNBn (350 mg, 2.986 mmol). After the purification by column chromatography on alumina, **2d** (380 mg, 0.782 mmol, 67%) was obtained as a dark red solid. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.25–7.00 (m, 10 H, *Ph*), 4.28 (dd, J = 16.8 Hz, 4 H, CH_2), 2.50 (q, J = 7.2 Hz, 2 H, CH_2), 1.73 (br. s, 15 H, Cp*-CH_3), 1.68 (t, J = 7.2 Hz, 3 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ =

3064 (vw), 3030 (vw), 2951 (w), 2907 (m), 2854 (vw), 2103 (vs), 2054 (vs), 2004 (vs), 1605 (vw), 1496 (m), 1454 (w), 1375 (w), 1348 (m), 1302 (vw), 1244 (w), 1029 (m), 801 (w), 733 (m), 697 (m), 598 (m), 508 (w) cm^{-1}. HRMS (EI): calcd. for $[M]^+$ 486.1792; found 486.1797. $C_{28}H_{34}FeN_2S$ (486.49): calcd. C 69.13, H 7.04, N 5.76; found C 69.14, H 7.06, N 5.77.

[Cp*FeCN*t*Bu(μ-CN*t*Bu)(μ-SEt)PdCl(PPh$_3$)][PF$_6$] (3a): A solution of $AgPF_6$ (92 mg, 0.364 mmol) in THF (2 mL) was added to a suspension of $[PdCl_2(PPh_3)_2]$ (250 mg, 0.356 mmol) in THF (10 mL) and the resulting solution was stirred for about 3 h. A solution of **2a** (152 mg, 0.364 mg) in THF (3 mL) was added to the reaction mixture, and the resulting violet-red suspension was stirred in the darkness at room temperature for 12 h. After filtration and removal of the solvent in vacuo, the residue was washed with Et_2O (2×10 mL) and then extracted with acetone. Addition of Et_2O to the concentrated acetone solution afforded **3a** (296 mg, 0.306 mmol, 84%) as a dark violet-red crystals. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.85–7.52 (m, 15 H, *Ph*), 1.95 (br. s, 15 H, Cp*-C*H*$_3$), 1.70 (s, 9 H, *t*Bu), 1.60 (s, 9 H, *t*Bu), 1.53 (q, *J* = 8.0 Hz, 2 H, C*H*$_2$), 0.81 (t, *J* = 8.0 Hz, 3 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone): δ = 30.2 (s, *P*Ph$_3$), –144.3 (sept, *P*F$_6$) ppm. IR (KBr): $\tilde{\nu}$ = 3057 (vw), 2980 (w), 2158 (s), 2124 (m), 1481 (w), 1437 (m), 1372 (vw), 1191 (w), 1097 (m), 842 (vs), 750 (w), 694 (m), 558 (m), 526 (m), 509 (vw), 472 (vw) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 821.1740; found 821.1747. $C_{44}H_{61}ClF_6FeN_2OP_2PdS$ (1039.69): calcd. C 50.83, H 5.91, N 2.69; found C 50.86, H 5.95, N 2.71.

[Cp*FeCNPh(μ-CNPh)(μ-SEt)PdCl(PPh$_3$)][PF$_6$] (3b): The reaction was carried out analogously to the procedures described for **3a** by treatment of **2b** (152 mg, 0.332 mmol) with $[PdCl_2(PPh_3)_2]$ (233 mg, 0.332 mmol) and $AgPF_6$ (87 mg, 0.344 mmol), and gave **3b** (306 mg, 0.304 mmol, 92%) as a dark violet-red crystals. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.85–7.47 (m, 25 H, *Ph*), 2.12 (br. s, 15 H, Cp*-C*H*$_3$), 1.82 (m, 1 H, C*H*$_2$), 1.61 (m, 1 H, C*H*$_2$), 0.87 (t, *J* = 8.0 Hz, 3 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone): δ = 31.0 (s, *P*Ph$_3$), –144.3 (sept, *P*F$_6$) ppm. IR (KBr): $\tilde{\nu}$ = 3061 (vw), 2924 (m), 2854 (w), 2125 (vs), 2112 (vs), 2060 (vs), 1631 (w), 1589 (m), 1482 (m), 1454 (w), 1435 (m), 1380 (m), 1161 (vw), 1096 (m), 1024 (w), 843 (vs), 759 (m), 693 (m), 558 (m), 529 (w), 519 (vw), 495 (vw) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 861.1114; found 861.1123. $C_{44}H_{45}ClF_6FeN_2P_2PdS$ (1007.56): calcd. C 52.45, H 4.50, N 2.78; found C 52.49, H 4.55, N 2.79.

[Cp*FeCNCy(μ-CNCy)(μ-SEt)PdCl(PPh$_3$)][PF$_6$] (3c): The reaction was carried out analogously to the procedures described for **3a** by treatment of **2c** (259 mg, 0.551 mmol) with $[PdCl_2(PPh_3)_2]$ (388 mg, 0.553 mmol) and $AgPF_6$ (140 mg, 0.553 mmol), and gave **3c** (488 mg, 0.479 mmol, 87%) as a dark violet-red crystals. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.85–7.54 (m, 15 H, *Ph*), 4.55 (t, *J* = 8.0 Hz, 1 H, C*H*), 4.28 (t, *J* = 8.0 Hz, 1 H, C*H*), 1.96 (br. s, 15 H, Cp*-C*H*$_3$), 1.79–1.29 (m, 20 H, *cyclo*-C$_6$*H*$_{11}$), 0.88 (q, *J* = 8.0 Hz, 2 H, C*H*$_2$), 0.79 (t, *J* = 8.0 Hz, 3 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone): δ = 29.7 (s, *P*Ph$_3$), –144.3 (sept, *P*F$_6$) ppm. IR (KBr): $\tilde{\nu}$ = 2934 (w), 2859 (vw), 2179 (vs), 2140 (vw), 2107 (vw), 1482 (w), 1436 (m), 1367 (w), 1096 (m), 1026 (vw), 840 (vs), 746 (w), 696 (m), 557 (m), 530 (m), 510 (m), 448 (vw) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 873.2053; found 873.2057. $C_{44}H_{57}ClF_6FeN_2P_2PdS$ (1019.66): calcd. C 51.83, H 5.63, N 2.75; found C 51.88, H 5.65, N 2.79.

[Cp*FeCNBn(μ-CNBn)(μ-SEt)PdCl(PPh$_3$)][PF$_6$] (3d): The reaction was carried out analogously to the procedures described for **3a** by treatment of **2d** (168 mg, 0.346 mmol) with $[PdCl_2(PPh_3)_2]$ (243 mg, 0.346 mmol) and $AgPF_6$ (88 mg, 0.348 mmol), and gave **3d** (333 mg, 0.322 mmol, 93%) as a dark violet-red crystals. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.76–7.41 (m, 25 H, *Ph*), 5.52 (dd, *J* = 16.0 Hz, 2 H, C*H*$_2$), 5.27 (dd, *J* = 16.0 Hz, 2 H, C*H*$_2$), 1.89 (br. s, 15 H, Cp*-C*H*$_3$), 1.52 (m, 1 H, C*H*$_2$), 1.36 (m, 1 H, C*H*$_2$), 0.55 (t, *J* = 8.0 Hz, 3 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone): δ = 29.4 (s, *P*Ph$_3$), –144.3 (sept, *P*F$_6$) ppm. IR (KBr): $\tilde{\nu}$ = 3049 (w), 2920 (w), 2169 (vs), 2086 (vs), 1496 (vw), 1481 (w), 1453 (w), 1435 (m), 1381 (w), 1347 (w), 1097 (m), 1026 (m), 840 (vs), 748 (w), 739 (w), 695 (m), 558 (m), 532 (m), 508 (m), 477 (vw), 450 (w) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 889.1427; found 889.1432. $C_{46}H_{49}ClF_6FeN_2P_2PdS$ (1035.62): calcd. C 53.35, H 4.77, N 2.70; found C 53.38, H 4.80, N 2.76.

[Cp*Fe(CN*t*Bu)$_2$(μ-SEt)NiCl(PPh$_3$)][PF$_6$] (4): A solution of $AgPF_6$ (101 mg, 0.399 mmol) in THF (4 mL) was added to a suspension of $[NiCl_2(PPh_3)_2]$ (250 mg, 0.382 mmol) in THF (15 mL) and the resulting solution was stirred for about 3 h. A solution of **2a** (160 mg, 0.383 mmol) in THF (5 mL) was added to the reaction mixture, and the resulting brown-yellow suspension was stirred in the darkness at room temperature for 12 h. After filtration and removal of the solvent in vacuo, the residue was washed with Et_2O (2×10 mL) and then extracted with acetone. Addition of Et_2O to the concentrated acetone solution afforded **4** (264 mg, 0.288 mmol, 75%) as a dark brown-yellow crystals. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 7.80–7.29 (m, 15 H, *Ph*), 2.59 (br. s, 15 H, Cp*-C*H*$_3$), 1.53 (br., 9 H, *t*Bu), 1.48 (br., 9 H, *t*Bu), 1.27 (br., 2 H, C*H*$_2$), 0.79 (br., 3 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD$_3$CN): δ = –5.9 (s, *P*Ph$_3$), –144.7 (sept, *P*F$_6$) ppm. IR (KBr): $\tilde{\nu}$ = 3056 (vw), 2979 (w), 2157 (vs), 2132 (vs), 1484 (m), 1458 (w), 1438 (m), 1372 (m), 1262 (w), 1190 (m), 1095 (m), 1023 (w), 840 (vs), 754 (m), 697 (m), 558 (s), 526 (s), 510 (m), 494 (w), 469 (w) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 773.2058; found 773.2065. $C_{40}H_{55}ClF_6FeN_2NiOP_2S$ (937.87): calcd. C 51.23, H 5.91, N 2.99; found C 51.24, H 5.93, N 3.01.

[{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$Au][PF$_6$] (5): A solution of $AgPF_6$ (110 mg, 0.435 mmol) in THF (4 mL) was added to a solution of $(Ph_3P)AuCl$ (215 mg, 0.434 mmol) in THF (8 mL) and stirred at 0 °C for about 1 h. A solution of **2a** (365 mg, 0.873 mmol) in THF (4 mL) was added to the reaction mixture, and the resulting dark brown-red suspension was stirred in the darkness at room temperature for 12 h. After removal of the solvent in vacuo, the residue was washed with Et_2O (3×8 mL) and then extracted with THF. Addition of Et_2O to the concentrated THF solution afforded **5** (263 mg, 0.223 mmol, 52%) as a dark brown-red crystals. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 2.34 (q, *J* = 8.0 Hz, 4 H, C*H*$_2$), 1.64 (br. s, 30 H, Cp*-C*H*$_3$), 1.51 (s, 36 H, *t*Bu), 1.28 (t, *J* = 8.0 Hz, 6 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD$_3$CN): δ = –144.7 (sept, *P*F$_6$) ppm. IR (KBr): $\tilde{\nu}$ = 2978 (m), 2922 (w), 2123 (vs), 2089 (vs), 2050 (vs), 1459 (m), 1398 (w), 1371 (m), 1235 (w), 1210 (m), 1028 (vw), 840 (vs), 557 (m), 536 (w), 486 (w) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 1033.3876; found 1033.3884. $C_{44}H_{76}AuF_6Fe_2N_4PS_2$ (1178.85): calcd. C 44.83, H 6.50, N 4.75; found C 44.86, H 6.57, N 4.79.

[{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$Ag][OTf] (6). Method A: A solution of AgOTf (84 mg, 0.327 mmol) in THF (5 mL) was added to a solution of **2a** (273 mg, 0.653 mmol) in THF (5 mL). The resulting brown-red solution was stirred in the darkness at room temperature for 12 h. After removal of the solvent in vacuo, the residue was washed with Et_2O (2×5 mL) and extracted with THF. Addition of Et_2O to the concentrated THF solution afforded **6** (287 mg, 0.263 mmol, 81%) as a dark brown-red crystals.

Method B: A solution of $(Ph_3P)AgOTf$ (192 mg, 0.370 mmol) in THF (5 mL) was added to a solution of **2a** (310 mg, 0.742 mmol) in THF (5 mL). The resulting violet-red solution was stirred in the darkness at room temperature for 12 h. After filtration and removal of the solvent in vacuo, the residue was washed with Et_2O (2×5 mL) and extracted with THF. Addition of Et_2O to the concentrated THF solution afforded **6** (166 mg, 0.152 mmol, 41%) as a dark brown-red crystals. ^1H NMR (400 MHz, CD_3CN): δ = 2.11 (br., 4 H, CH_2), 1.60 (br., 30 H, Cp*-CH_3), 1.49 (s, 36 H, *t*Bu), 1.25 (br., 6 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2975 (m), 2914 (w), 2114 (vs), 2052 (vs), 1456 (m), 1369 (m), 1272 (vs), 1207 (m), 1144 (m), 1031 (s), 741 (w), 638 (s), 535 (vw), 516 (w) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 943.3261; found 943.3265. $C_{45}H_{76}AgF_3Fe_2N_4O_3S_3$ (1093.86): calcd. C 49.41, H 7.00, N 5.12; found C 49.46, H 7.06, N 5.17.

[{Cp*Fe(CN*t*Bu)$_2$(μ-SEt)}$_2$Cu][PF$_6$] (7). Method A: A solution of $AgPF_6$ (134 mg, 0.530 mmol) in THF (5 mL) was added to a solution of $(Ph_3P)CuCl$ (188 mg, 0.521 mmol) in THF (15 mL) and stirred for about 2 h. A solution of **2a** (438 mg, 1.048 mmol) in THF (5 mL) was added to the reaction mixture, and the resulting dark red suspension was stirred in the darkness at room temperature for 12 h. After removal of the solvent in vacuo, the residue was washed with Et_2O (2×5 mL) and then extracted with THF. Addition of Et_2O to the concentrated THF solution afforded **7** (406 mg, 0.389 mmol, 74%) as a dark brown-red crystals.

Method B: A solution of $[CuPF_6(CH_3CN)_4]$ (115 mg, 0.308 mmol) in THF (8 mL) was added to a solution of **2a** (258 mg, 0.617 mmol) in THF (2 mL). The resulting brown-red solution was stirred in the darkness at room temperature for 12 h. After removal of the solvent in vacuo, the residue was washed with Et_2O (2×5 mL) and extracted with THF. Addition of Et_2O to the concentrated THF solution afforded **7** (275 mg, 0.263 mmol, 86%) as a dark brown-red crystals. ^1H NMR (400 MHz, CD_3CN): δ = 2.07 (q, *J* = 7.2 Hz, 4 H, CH_2), 1.61 (br. s, 30 H, Cp*-CH_3), 1.48 (s, 36 H, *t*Bu), 1.23 (t, *J* = 7.2 Hz, 6 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ = –144.7 (sept, PF_6) ppm. IR (KBr): $\tilde{\nu}$ = 2978 (m), 2920 (w), 2119 (vs), 2051 (vs), 1460 (m), 1371 (m), 1235 (w), 1210 (m), 1071 (vw), 1028 (w), 840 (vs), 770 (w), 743 (w), 557 (m), 536 (w), 482 (m) cm^{-1}. HRMS (ESI): calcd. for $[M - PF_6]^+$ 899.3506; found 899.3509. $C_{44}H_{76}CuF_6Fe_2N_4PS_2$ (1045.43): calcd. C 50.55, H 7.33, N 5.36; found C 50.56, H 7.37, N 5.39.

X-ray Data Collection and Structure Refinement: The data were obtained with a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Empirical absorption corrections were performed using the SADABS program.[18] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 using SHELX97.[19] All of the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogen atoms were fitted geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms with the isotropic displacement being fixed at 1.2 and 1.5 times the aromatic and methyl carbon atoms that attached, respectively. The SEt ligand in **4**, and one of CN*t*Bu ligands in **5**, **6**, and **7** were disordered and restrained during refinement of the structure. Disordered atomic positions were split into two parts and refined using one occupancy parameter per disordered group. Crystal data and collection details for the X-ray structure determinations are summarized in Table 4.

CCDC-773332 (for **3a**), -773333 (for **3b**), -773334 (for **3c**), -773335 (for **3d**), -773336 (for **4**), -773337 (for **7**), -773338 (for **6**) and -773339 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ORTEP drawings of complexes **3c** and **3d**. The ^1H NMR and IR spectra of complexes **2**, **3**, **4**, **5**, **6**, and **7**. The $^{31}P\{^1H\}$ NMR spectra of complexes **3** and **4**.

Table 4. Crystal data and structure refinements for **3a**, **3b**, **4**, **5**, **6**, and **7**.

	3a·THF	**3b**	**4**·H_2O	**5**	**6**	**7**
Empirical formula	$C_{44}H_{61}ClF_6FeN_2OP_2PdS$	$C_{44}H_{45}ClF_6FeN_2P_2PdS$	$C_{40}H_{55}ClF_6FeN_2NiOP_2S$	$C_{44}H_{76}AuF_6Fe_2N_4PS_2$	$C_{45}H_{76}AgF_3Fe_2N_4O_3S_3$	$C_{44}H_{76}CuF_6Fe_2N_4PS_2$
Formula weight	1039.65	1007.52	937.87	1178.84	1093.85	1045.42
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal size [mm]	0.59×0.36×0.24	0.35×0.14×0.10	0.23×0.21×0.18	0.41×0.26×0.15	0.78×0.64×0.24	0.35×0.26×0.18
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.6205(17)	9.223(3)	11.600(5)	9.289(4)	9.347(4)	9.216(6)
b [Å]	19.828(3)	27.678(9)	19.788(8)	11.200(4)	11.274(5)	11.158(7)
c [Å]	21.404(3)	18.199(6)	21.125(9)	14.281(5)	14.401(6)	14.292(9)
β [°]	94.457(9)	101.133(6)	94.560(6)	76.333(4)	77.255(4)	76.323(10)
V [$Å^3$]	4916.6(12)	4558(3)	4833(4)	1348.3(9)	1382.5(10)	1329.2(14)
Z	4	4	4	1	1	1
d_c [$g cm^{-3}$]	1.405	1.468	1.289	1.452	1.314	1.306
μ [mm^{-1}]	0.879	0.944	0.907	3.404	1.029	1.097
F(000)	2144	2048	1952	600	572	550
θ_{max} [°]	26.25	25.00	25.00	26.67	25.00	25.00
Reflections collected	25017	21999	23881	6724	6730	6503
Reflections unique	8601	8010	8507	4637	4728	4616
R_{int}	0.0450	0.0508	0.0589	0.0256	0.0187	0.0163
GOF(F^2)	1.051	1.062	0.992	1.027	1.059	1.057
R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0526, wR_2 = 0.1166	R_1 = 0.0448, wR_2 = 0.1077	R_1 = 0.0684, wR_2 = 0.1876	R_1 = 0.0474, wR_2 = 0.1200	R_1 = 0.0357, wR_2 = 0.0982	R_1 = 0.0619, wR_2 = 0.2003
R indices (all data)[b]	R_1 = 0.0825, wR_2 = 0.1262	R_1 = 0.0683, wR_2 = 0.1175	R_1 = 0.1210, wR_2 = 0.2127	R_1 = 0.0572, wR_2 = 0.1250	R_1 = 0.0428, wR_2 = 0.1025	R_1 = 0.0806, wR_2 = 0.2173
Residuals [$e Å^{-3}$]	0.889/–0.497	0.606/–0.515	0.692/–0.430	1.491/–1.691	0.513/–0.399	1.608/–0.640

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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