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Article

Bimetallic Clusters of Iron with Palladium and Platinum. Synthesis and Structures of $Fe_2(CO)_9[M(PBu^t{}_3)]_2$ (M = Pd or Pt) and $Fe_2(CO)_8[Pt(PBu^t{}_3)]_2(\mu\text{-}H)_2$

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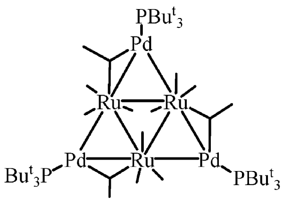
The reaction of $Fe_2(CO)_9$ with $Pd(PBu^t{}_3)_2$ and $Pt(PBu^t{}_3)_2$ yielded the Fe–Pd and Fe–Pt cluster complexes $Fe_2(CO)_9[M(PBu^t{}_3)]_2$, M = Pd (**8**) or Pt (**9**). The structures of **8** and **9** are analogous and consist of nearly planar butterfly clusters of two palladium/platinum atoms in the wing-tip positions and two mutually bonded iron atoms, Fe–Fe = 2.9582(11) Å in **8** and 2.9100 (9) Å in **9**. Compound **8** decomposes to form the mononuclear iron compound $Fe(CO)_4(PBu^t{}_3)$ (**11**) when heated at 68 °C. The reaction of $Pt(PBu^t{}_3)_2$ with $Fe_2(CO)_9$ in the presence of hydrogen at 127 °C yielded the dihydrido complex $Fe_2(CO)_8[Pt(PBu^t{}_3)]_2(\mu\text{-}H)_2$ (**10**). Compound **10** contains a closed Fe_2Pt_2 tetrahedral cluster with hydrido ligands bridging two of the Fe–Pt bonds. Compounds **8**, **9**, and **10** were structurally characterized crystallographically.

Introduction

Recent studies have shown that heterometallic nanoparticles containing palladium or platinum exhibit better catalytic properties than the individual components.[1] Mixed-metal cluster complexes have been shown to produce more intimately mixed bimetallic heterogeneous catalysts than those prepared by coimpregnation methods.[2] A variety of di- and polynuclear metal cluster complexes have been prepared in the past couple of decades.[3] In recent studies, we have shown that the compounds $M(PBu^t{}_3)_2$, M = Pd or Pt, are very effective reagents for preparing heteronuclear cluster complexes by adding bridging $M(PBu^t{}_3)$ groups across metal−metal bonds.[4,5] Examples of some of these products include $Ru_3(CO)_{12}[Pd(PBu^t{}_3)]_3$ (**1**), $Ru_6(CO)_{17}(\mu_6\text{-}C)[Pd(PBu^t{}_3)]_2$ (**2**),[4a] and $MRu_5(CO)_{15}(PBu^t{}_3)(C)$ (**3**, M = Pt; **4**, M = Pd).[5]



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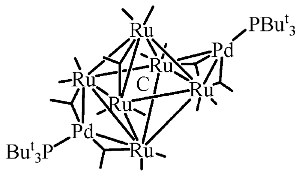

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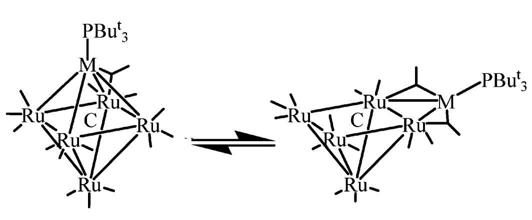
Interestingly, compounds **3** and **4** both exist in solution as a mixture of two isomers, a closed form **A** and an open form **B**, that interconvert rapidly on the NMR time scale.



A **B**

We have shown that $Pd(PBu^t{}_3)_2$ and $Pt(PBu^t{}_3)_2$ both react with $Ru(CO)_5$ to yield the tetranuclear compounds $Ru_2(CO)_9$-

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(1) (a) Thomas, J. M.; Raja, R.; Lewis, W. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 6456. (b) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. *Acc. Chem. Res.* **2003**, *36*, 20. (c) Thomas, J. M.; Raja, R.; Johnson, B. F. G.; Hermans, S.; Jones, M. D.; Khimyak, T.; *Ind. Eng. Chem. Res.* **2003**, *42*, 1563. (c) Johnson, B. F. G. *Top. Catal.* **2003**, *24*, 147.

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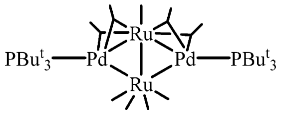
$[M(PBu^t_3)]_2$ (**5**, M = Pd; **6**, M = Pt) and the trinuclear Ru_2-Pt compound $Ru_2(CO)_9[Pt(PBu^t_3)]$ (**7**) that have $Pd(PBu^t_3)$ or $Pt(PBu^t_3)$ groups bridging the Ru−Ru bond.[6]



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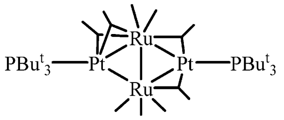

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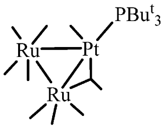

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We have recently shown that platinum−iron catalysts derived from platinum−iron cluster complexes are superior to catalysts prepared by coimpregnation methods for preferential oxidation of CO in the presence of hydrogen, a reaction that is important in the purification of hydrogen.[2a] Herein, we describe our investigations of the reactions of $Fe_2(CO)_9$ with $Pd(PBu^t_3)_2$ and $Pt(PBu^t_3)_2$ which have yielded the new palladium− and platinum−iron complexes $Fe_2(CO)_9[M(PBu^t_3)]_2$ (**8**, M = Pd; **9**, M = Pt). Both these compounds are analogues of **5**. Additionally, the reaction of $Pt(PBu^t_3)_2$ with $Fe_2(CO)_9$, in the presence of hydrogen has afforded the new dihydrido compound $Fe_2(CO)_8[Pt(PBu^t_3)]_2(\mu\text{-}H)_2$ (**10**) which can also be obtained from the reaction of **9** with hydrogen. The structures of compounds **8**, **9**, and **10** were established crystallographically.

Experimental Section

General Data. Reagent-grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ^1H NMR and $^{31}P\{^1H\}$ NMR were recorded on a Varian Mercury 400 spectrometer operating at 400.1 and 161.9 MHz, respectively. $^{31}P\{^1H\}$ NMR spectra were externally referenced against 85% *ortho*-H_3PO_4. $Pd(PBu^t_3)_2$, $Pt(PBu^t_3)_2$, and $Fe_2(CO)_9$ were obtained from STREM and were used without further purification. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Preparation of $Fe_2(CO)_9[Pd(PBu^t_3)]_2$ (8). Under an atmosphere of nitrogen, $Pd(PBu^t_3)_2$ (38.0 mg, 0.074 mmol) was added to a suspension of $Fe_2(CO)_9$ (8.8 mg. 0.024 mmol) in 30 mL of hexane. The color of the solution turned to green immediately. The solution was then stirred for 4.5 h at room temperature, after which the solution was quickly filtered through a silica gel column eluting with CH_2Cl_2 to yield 20.0 mg (84% based on Fe) of green **8** which can be crystallized from hexane/methylene chloride solutions by cooling to −25 °C. Note: compound **8** slowly decomposes on silica gel. Spectral data for **8**. IR ν_{CO} (cm^{-1} in hexane): 2007 (s), 1971 (m), 1952 (w), 1927 (w), 1917 (w), 1872 (m). ^1H NMR (toluene-d_8 at 25 °C in ppm): 1.30 (d, $^3J_{P-H}$ = 13 Hz, 54H, CH_3). $^{31}P\{^1H\}$ NMR (toluene-d_8 at 25 °C in ppm): 78.5 (s, 1p). Anal. Calcd: C 40.39, H 5.54. Found: C 39.78, H 5.04.

Reaction of $Fe_2(CO)_9$ with $Pt(PBu^t_3)_2$. $Fe_2(CO)_9$ (20.1 mg, 0.055 mmol) and $Pt(PBu^t_3)_2$ (73.5 mg, 0.123 mmol) were dissolved in 20 mL of CH_2Cl_2 and stirred at room temperature for 1 h. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and separated by TLC using a 4:1 hexane/methylene chloride solvent mixture to give in order of elution, a light-yellow band of $Fe(CO)_4(PBu^t_3)$ (**11**, 3.1 mg, 8% based on Fe), a red band of $Fe_2(CO)_9[Pt(PBu^t_3)]$[6] (**12**, 19.2 mg, 46% based on Fe), a green band of $Fe_2(CO)_9[Pt(PBu^t_3)]_2$ (**9**, 1.3 mg, 2% based on Fe), and a yellow band of $Pt_3(PBu^t_3)_3(CO)_3$[7] (6.0 mg, 11% based on Pt). Note: compound **9** slowly decomposes on silica gel. Spectral data for **9**. IR ν_{CO} (cm^{-1} in hexane): 2073 (w), 2048 (m), 2021 (m), 2003 (s), 1989 (vs), 1980 (s, sh), 1895 (w, br), 1861 (w, br), 1811 (m). ^1H NMR(toluene-d_8 at 25 °C in ppm): 1.33 (d, $^3J_{P-H}$ = 13 Hz, 54H, CH_3). $^{31}P\{^1H\}$ NMR (toluene-d_8 at 25 °C in ppm): 113.4 (s, $^1J_{Pt-P}$ = 5054 Hz, 2p).

Preparation of $Fe_2(CO)_8[Pt(PBu^t_3)]_2(\mu\text{-}H)_2$ (10). To a suspension of $Fe_2(CO)_9$ (15.0 mg. 0.041 mmol) in 30 mL of octane, $Pt(PBu^t_3)_2$ (75.3 mg, 0.126 mmol) was added. The solution was then purged with hydrogen (1 atm) for 45 min at 127 °C (octane reflux). The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and separated by TLC using a 3:1 hexane/methylene chloride solvent mixture to give a dirty-green-colored band of **10** (22.3 mg, 48%). Spectral data for **10**. IR ν_{CO} (cm^{-1} in hexane): 2040 (m) 2015 (vs), 2007(s), 1982 (s), 1955 (m), 1930 (m). ^1H NMR (toluene-d_8 at 25 °C in ppm): 1.21 (d, $^3J_{P-H}$ =13 Hz, 54H, CH_3), −10.98 (t, $^1J_{Pt-H}$ = 568 Hz, J_{P-H} = 8 Hz, 2H, hydride). $^{31}P\{^1H\}$ NMR (toluene-d_8 at 25 °C in ppm): 104.9 (s, $^1J_{Pt-P}$ = 2774 Hz, $^3J_{Pt-P}$ = 145 Hz, $^4J_{P-P}$ = 9 Hz, 2P). Anal. Calcd: C 33.94, H 4.98. Found: C 33.95, H 4.79.

Thermolysis of 8. A solution of **8** (29.5 mg, 0.030 mmol) in 30 mL of hexane was heated to reflux for 45 min. The color of the solution turned from green to colorless with formation of a black precipitate, presumably palladium metal. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and separated by TLC using a 4:1 hexane/methylene chloride solvent mixture to give a light-yellow band of $Fe(CO)_4(PBu^t_3)$ (7.0 mg, 31%).

Conversion of 12 to 9. To **12** (8.0 mg, 0.011 mmol) dissolved in 15 mL of CH_2Cl_2 was added $Pt(PBu^t_3)_2$ (20.0 mg, 0.033 mmol). The solution was stirred at room temperature for 3 h after which the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and separated by TLC using a 3:1 hexane/methylene chloride solvent mixture to give unreacted **12** (5.0 mg, 63%), green **9** (0.9 mg, 7%), and yellow $Pt_3(PBu^t_3)_3(CO)_3$ (4.0 mg, 28% based on Pt).

Addition of H_2 to 9. Compound **9** (6.0 mg, 0.005 mmol) was dissolved in 15 mL of CH_2Cl_2. With stirring, hydrogen gas was passed through the solution at room temperature for 1.5 h. The solvent was then removed in vacuo, and the residue was dissolved in CH_2Cl_2 and separated by TLC using a 3:1 hexane/methylene chloride solvent mixture to give red **12** (1.0 mg, 25%) and **10** (2 mg, 34%).

Preparation of 10 at 68 °C. To a suspension of $Fe_2(CO)_9$ (14.6 mg. 0.040 mmol) in 30 mL of hexane, $Pt(PBu^t_3)_2$ (71.6 mg, 0.120 mmol) was added. The solution was then purged with hydrogen (1 atm) for 1.5 h at 68 °C (hexane reflux). The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and separated

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Table 1. Crystallographic Data for Compounds **8**, **9**, and **10**

	8	**9**	**10**
empirical formula	$Pd_2Fe_2P_2O_9C_{33}H_{54}$	$Pt_2Fe_2P_2O_9C_{33}H_{54}$	$Pt_2Fe_2P_2O_8C_{32}H_{56}$
fw	981.2	1158.58	1132.59
cryst syst	triclinic	orthorhombic	triclinic
lattice params			
a (Å)	8.6883(5)	27.9770(11)	10.5572(5)
b (Å)	15.1816(9)	12.0751(4)	13.6856(6)
c (Å)	16.6547(9)	11.9252(4)	14.6635(7)
α (deg)	106.409(1)	90	95.812(1)
β (deg)	101.531(1)	90	95.047(1)
γ (deg)	96.266(1)	90	107.863(1)
V (Å^3)	2032.5(2)	4028.6(2)	1990.19(16)
space group	$P\bar{1}$ (No. 2)	$Pca2_1$(No. 29)	$P\bar{1}$ (No. 2)
Z value	2	4	2
ρ_{calc} (g/cm^3)	1.603	1.910	1.890
μ (Mo Kα) (mm^{-1})	1.695	7.755	7.845
temp (K)	294	294	294
$2\Theta_{max}$ (°)	52.04	56.70	56.60
no. obs. ($I > 2\sigma(I)$)	6684	8916	8735
no. params	451	451	441
GOF	1.18	0.931	1.039
max. shift in cycle	0.003	0.004	0.003
residuals^a: R; R_w	0.0463; 0.1140	0.0254; 0.0556	0.0237; 0.0591
abs correction, max/min	multiscan 1.000/0.862	multiscan 1.000.0.675	multiscan 1.000/0.548
largest peak in final diff. Map (e$^-$/Å^3)	1.278	0.932	0.908

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

by TLC using a 3:1 hexane/methylene chloride solvent mixture to give **10** (13.7 mg, 30%).

Crystallographic Analyses. Dark single crystals of **8**, **9**, and **10** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane/methylene chloride solvent mixture at −25 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[8] Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[9] Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Compounds **8** and **10** crystallized in the triclinic crystal system. For both compounds, the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All the nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and refined as standard riding atoms. For compound **10**, the two hydrido ligands were located and refined successfully with isotropic thermal parameters.

Compound **9** crystallized in the orthorhombic crystal system. The two possible space groups, $Pca2_1$ and $Pbcm$, were identified on the basis of the patterns of systematic absences in the data. On the basis of the mean value of $|E^2 - 1|$ for all reflections, where E is a normalized structure factor, the non-centrosymmetric space group $Pca2_1$ was chosen and confirmed by the successful refinement of the structure. Also, attempts to solve the structure in $Pbcm$ were unsuccessful. All the nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and refined as standard riding atoms.

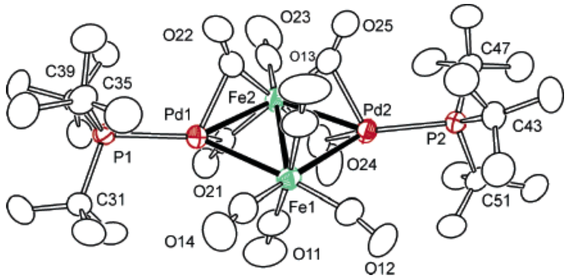
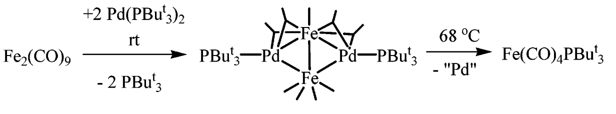


Figure 1. ORTEP diagram of $Fe_2(CO)_9[Pd(PBu^t{}_3)]_2$ (**8**) showing 40% probability thermal ellipsoids.

Results and Discussion

The dipalladium−diiron compound **8** was obtained in 84% yield from the reaction of $Fe_2(CO)_9$ and $Pd(PBu^t{}_3)_2$ at room temperature, see eq 1. Compound **8** was characterized by a combination of IR, ^{1}H and ^{31}P NMR, single-crystal X-ray diffraction, and elemental analyses. An ORTEP diagram of the molecular structure of **8** is shown in Figure 1. Selected bond distances and angles are listed in Table 2.



8

(1)

The structure of compound **8** is analogous to the ruthenium compound **5**.[6] Compound **8** consists of a butterfly cluster of two palladium atoms and two iron atoms. The distance between the two iron atoms is short enough to indicate the presence of direct metal−metal bonding, Fe(1)−Fe(2) = 2.9582(11) Å, but there is clearly no direct bonding between the two palladium atoms, Pd···Pd = 4.4816(6) Å. There are

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(8) *SAINT+*, Version 6.02a; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(9) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

Table 2. Selected Intramolecular Bond Distances and Angles for Compound **8**[a]

atom	atom	distance(Å)	atom	atom	distance(Å)
Pd(1)	Fe(1)	2.7119(9)	Fe(2)	C(22)	1.907(7)
Pd(1)	Fe(2)	2.6490(9)	Pd(1)	C(21)	2.097(6)
Pd(2)	Fe(1)	2.7356(10)	Fe(2)	C(21)	1.891(6)
Pd(2)	Fe(2)	2.6508(9)	Pd(2)	C(24)	2.096(7)
Fe(1)	Fe(2)	2.9582(11)	Fe(2)	C(24)	1.891(7)
Pd(1)	P(1)	2.4003(15)	Pd(2)	C(25)	2.104(6)
Pd(2)	P(2)	2.4071(15)	Fe(2)	C(25)	1.907(7)
Pd(1)	C(22)	2.102(6)			

atom	atom	atom	angle(deg)	atom	atom	atom	angle(deg)
Pd(1)	Fe(1)	Pd(2)	110.71(3)	Fe(2)	Pd(2)	Fe(1)	66.60(3)
Pd(2)	Fe(2)	Pd(1)	115.48(3)	P(1)	Pd(1)	Fe(2)	145.56(4)
Fe(2)	Pd(1)	Fe(1)	66.97(3)	P(2)	Pd(2)	Fe(1)	147.15(4)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

four carbonyl ligands bonded to Fe(1), all of which are terminal. There are five carbonyl ligands attached to Fe(2), but only one of these, C(23)−O(23), is terminal while the other four are bridges across the Fe−Pd bonds. The Fe(2)−Pd bond distances of 2.6490(9) and 2.6508(9) Å, are both significantly shorter than the Fe(1)−Pd bond distances, 2.7119(9) and 2.7356(10) Å, probably because of the presence of the bridging CO ligands across the Fe(2)−Pd bonds. Because there was no loss of a CO ligand during the course of the reaction, compound **8** can be viewed as a dipalladium adduct of rearranged form of the compound $Fe_2(CO)_9$. $Fe_2(CO)_9$ contains three bridging carbonyl ligands across its Fe−Fe bond,[10] while there are no bridging CO ligands across the Fe−Fe bond in **8**. The Fe−Fe bond distance in **8**, 2.9582(11) Å, is much longer than the Fe−Fe bond distance in $Fe_2(CO)_9$, 2.523(1) Å,[10] and in the diiron-platinum cluster complex **12**, 2.7188(6) Å.[6] Compound **8** contains a total of 58 cluster valence electrons, which is four electrons less than the number, 62, expected for a butterfly cluster where all the metal atoms have 18-electron configurations.[11] However, if both palladium atoms were considered to have 16-electron configurations, which is not uncommon for palladium, then the 58 electron count would be satisfactory. Molecular orbital calculations of **5** showed the presence of delocalized metal−metal bonding consisting of two three-center two-electron metal−metal bonds.[6] Because of its very similar structure, it can be assumed that a similar bonding model would be applicable to **8**. We found no evidence for the formation of a stable monopalladium adduct of $Fe_2(CO)_9$, $Fe_2(CO)_9[Pd(PBu^t_3)]$.

In solution, compound **8** decomposes in air at room temperature within a few hours. The decomposition products could not be characterized. However, when a solution of **8** was heated to 68 °C, compound **8** decomposed with formation of the mononuclear iron compound **11** in 31% yield and, presumably, Pd metal. Compound **11** was identified by its IR spectrum[12] and the unit cell dimensions of its crystalline form.[13] Compound **11** was previously synthesized from $Fe(CO)_5$ and PBu^t_3 but requires UV irradiation for 8 h.[12]

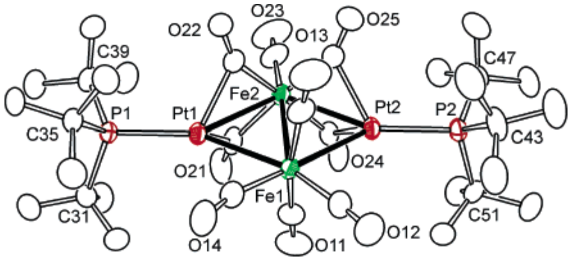

Figure 2. ORTEP diagram of $Fe_2(CO)_9[Pt(PBu^t_3)]_2$ (**9**) showing 40% probability thermal ellipsoids.

Table 3. Selected Intramolecular Bond Distances and Angles for Compound **9**[a]

atom	atom	distance(Å)	atom	atom	distance(Å)
Pt(1)	Fe(1)	2.7211(6)	Fe(2)	C(22)	1.902(5)
Pt(1)	Fe(2)	2.6669(7)	Pt(1)	C(21)	2.082(5)
Pt(2)	Fe(1)	2.7508(7)	Fe(2)	C(21)	1.916(6)
Pt(2)	Fe(2)	2.6422(7)	Pt(2)	C(24)	2.040(5)
Fe(1)	Fe(2)	2.9100(9)	Fe(2)	C(24)	1.910(5)
Pt(1)	P(1)	2.3293(11)	Pt(2)	C(25)	2.131(6)
Pt(2)	P(2)	2.3181(12)	Fe(2)	C(25)	1.876(6)
Pt(1)	C(22)	2.099(5)			

atom	atom	atom	angle(deg)	atom	atom	atom	angle(deg)
Pt(1)	Fe(1)	Pt(2)	111.89(2)	Fe(2)	Pt(2)	Fe(1)	65.276(19)
Pt(2)	Fe(2)	Pt(1)	117.28(2)	P(1)	Pt(1)	Fe(2)	141.59(3)
Fe(2)	Pt(1)	Fe(1)	65.371(19)	P(2)	Pt(2)	Fe(1)	145.85(3)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

The diplatinum−diiron compound **9** was obtained from the reaction of $Fe_2(CO)_9$ and $Pt(PBu^t_3)_2$ at room temperature. However, it was obtained only in a very low yield (2%), and all efforts to increase the yield by the addition of additional quantities of $Pt(PBu^t_3)_2$ were unsuccessful. This is due in part to its instability; it decomposes readily to the known triplatinum compound $Pt_3(PBu^t_3)_3(CO)_3$.[7] Compound **9** was characterized by a combination of IR, ^1H and ^{31}P NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **9** is shown in Figure 2. Selected bond distances and angles are listed in Table 3. The structure of compound **9** is analogous to that of compound **8**. The iron−iron bond in **9**, Fe(1)−Fe(2) = 2.9100(9) Å, is significantly shorter, 0.048(1) Å, than the iron−iron bond in **8**. The reason for the shortness of this bond in **9** compared to **8** is not apparent. Interestingly, the Ru−Ru bond distance in **6** is about 0.04 Å shorter than the Ru−Ru bond distance in **5**.

The reaction of $Fe_2(CO)_9$ and $Pt(PBu^t_3)_2$ with hydrogen (1 atm) at 127 °C afforded the tetranuclear dihydrido cluster complex **10** in 48% yield. Compound **10** was characterized by a combination of IR, ^1H and ^{31}P NMR, single-crystal X-ray diffraction, and elemental analyses. An ORTEP diagram of the molecular structure of **10** is shown in Figure 3. Selected bond distances and angles are listed in Table 4. The structure of compound **10** is analogous to the Ru_2Pt_2 cluster $Ru_2(CO)_8[Pt(PBu^t_3)]_2(\mu\text{-}H)_2$ **13**.[6] The molecule contains a cluster of four metal atoms, Fe_2Pt_2, in a closed tetrahedral shape. There are four Pt−Fe bonds, one Fe−Fe

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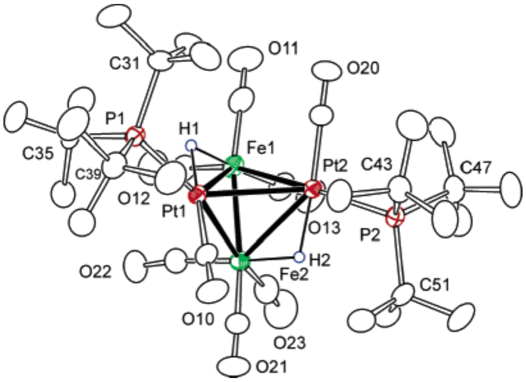


Figure 3. ORTEP diagram of $Fe_2(CO)_8[Pt(PBu^t_3)]_2(\mu\text{-}H)_2$ (**10**) showing 40% probability thermal ellipsoids.

Table 4. Selected Intramolecular Bond Distances and Angles for Compound **10**[a]

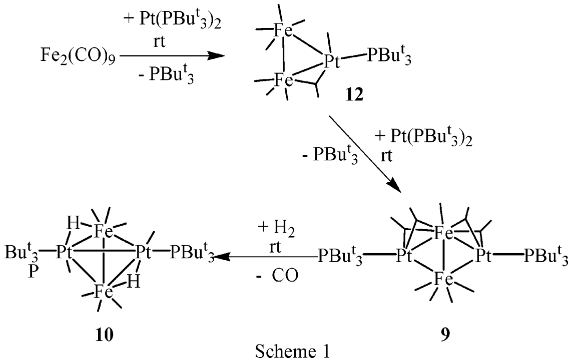
atom	atom	distance(Å)	atom	atom	distance(Å)
Pt(1)	Pt(2)	3.01992(19)	Pt(1)	P(1)	2.3808(7)
Pt(1)	Fe(1)	2.7361(5)	Pt(2)	P(2)	2.3741(8)
Pt(1)	Fe(2)	2.6384(4)	Pt(1)	H(1)	1.76(4)
Pt(2)	Fe(1)	2.6337(5)	Fe(1)	H(1)	1.72(4)
Pt(2)	Fe(2)	2.7267(4)	Pt(2)	H(2)	1.75(4)
Fe(1)	Fe(2)	2.5737(7)	Fe(2)	H(2)	1.68(4)

atom	atom	atom	angle(deg)	atom	atom	atom	angle(deg)
Fe(2)	Pt(1)	Fe(1)	57.190(15)	Pt(2)	Fe(1)	Fe(2)	63.137(14)
Fe(2)	Pt(1)	Pt(2)	57.140(10)	Pt(2)	Fe(1)	Pt(1)	68.413(11)
Fe(1)	Pt(1)	Pt(2)	54.187(10)	Fe(2)	Fe(1)	Pt(1)	59.495(14)
Fe(1)	Pt(2)	Fe(2)	57.358(15)	Pt(1)	Fe(2)	Fe(1)	63.314(14)
Fe(1)	Pt(2)	Pt(1)	57.400(11)	Pt(1)	Fe(2)	Pt(2)	68.489(11)
Fe(2)	Pt(2)	Pt(1)	57.371(10)	Fe(1)	Fe(2)	Pt(2)	59.504(14)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

bond, and one Pt−Pt bond. Two of the Fe−Pt bonds have bridging hydride ligands. The hydride ligands were located and refined successfully in the structural analysis. Each iron atom has three terminal CO ligands, and each platinum atom has one terminal CO ligand. The PBu^t_3 ligands are bonded to the platinum atoms. As expected, the hydride-bridged Fe−Pt bond distances, Fe(1)−Pt(1) = 2.7361(5) Å and Fe(2)−Pt(2) = 2.7267(4) Å, are significantly longer than the nonbridged Fe−Pt bond distances, Fe(1)−Pt(2) = 2.6337(5) Å and Fe(2)−Pt(1) = 2.6384(4) Å.[14] The two hydrido ligands are equivalent and appropriately show a single resonance in the ^1H NMR spectrum, $\delta = -10.98$ (t, $^1J_{Pt-H} = 568$ Hz, $J_{P-H} = 8$ Hz). All the metal−metal bond distances in **10** are similar to those found in the related triphenylphosphine compound $Fe_2(CO)_8[Pt(PPh_3)]_2(\mu\text{-}H)_2$.[15] Compound **10** contains 58 cluster valence electrons. It is, thus, isoelectronic with **9**, but it has, instead, a closed tetrahedral structure for the cluster, while the cluster of **9** is open. We have recently studied the compound $Cp_2Mo_2(CO)_4[Pt(PBu^t_3)]_2$, **14** which contains an open "butterfly" tetrahedral cluster of the four metal atoms.[16] While geometry-optimized DFT calculations confirmed this structure, they also revealed the presence of a second low-energy structure with a much shorter Pt−Pt distance that could be described as a closed tetrahedral structure. Curiously, the palladium homologue of **14**, $Cp_2Mo_2(CO)_4[Pd(PBu^t_3)]_2$, **15**, actually exhibits such a closed tetrahedral form for its ground-state structure.[16] The conclusion of this study was that the energy differences between the open and closed structures of the clusters are very small when they contain two Pd or Pt metal atoms, and it will be very difficult to predict the structure, a priori. There are other examples of 58 electron tetrahedral cluster complexes containingplatinum.[3d,6,15,17]

Scheme 1



A possible reaction pathway for the formation of **10** is shown in Scheme 1. The addition of one $Pt(PBu^t_3)$ group across the Fe−Fe bond of $Fe_2(CO)_9$ forms the trinuclear compound **12** after an opening of the CO bridges. This we have reported previously.[6] The next step is the addition of a second $Pt(PBu^t_3)$ group to give the tetranuclear compound **9**. This step is supported by the fact that compound **12** reacts with $Pt(PBu^t_3)_2$ to give **9**. Addition of 1 equiv of hydrogen to **9** accompanied by the loss of one CO ligand can then yield **10**. This is similar to the way **13** was obtained from the reaction of **5** with H_2.[6] This was established independently by the reaction of hydrogen with **9** to yield **10**. However, with the hydrogen addition reaction, there is a competing side reaction involving loss of a $Pt(PBu^t_3)$ group from **9** to yield **12** (25%). We were unable to synthesize the palladium analogue of **10** because compound **8** decomposed to the mononuclear compound **11** when heated in the presence of hydrogen.

The new Fe−Pd and Fe−Pt bimetallic clusters reported in this study should be useful precursors for the preparation of new heterogeneous nanoscale catalysts on supports.[2a]

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Supporting Information Available: Crystallographic data in txt format. This material is available free of charge via the Internet at http://pubs.acs.org.

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