Gold(I) Complexes

DOI: 10.1002/ange.200806012

Hexa- and Octagold Chains from Flexible Tetragold Molecular Units Supported by Linear Tetraphosphine Ligands**

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Gold nanoclusters and nanoparticles have been successfully applied to the development of chemical and biochemical sensing systems, optical and electronic devices, and catalytic reactions, by using the "bottom-up" approach to nanostructured inorganic–organic/biological hybrid materials.[1] In such systems, the gold nanoclusters and nanoparticles are spherical, any other dimensional and topological structure units are difficult to synthesize.[1e] In this context, 1D molecular gold chains are an important goal in the development of molecular wires. Interest in gold(I) complexes has recently increased because of their photophysical properties; they can also exhibit linearly assembled crystal structures with Au···Au separations of 2.7–3.3 Å, which result from weak, closed-shell aurophilic interactions.[1a,2–4] Single methylene-bridged di- and tridentate phosphines, such as dppm (bis(diphenylphosphino)methane) and dpmp (bis(diphenylphosphinomethyl)-phenylphosphine) were identified for the formation of molecular linear gold(I) chains, as they are known to be very effective in stabilizing photochemical and catalytically active multimetallic centers.[5–7] However, progress in this direction has not been great in the last decade, owing to the difficulty of synthesizing single methylene-bridged polydentate phosphine ligands, although multinuclear complexes supported by tetradentate phosphine ligands with ethylene and longer methylene chains have been prepared and exhibited interesting synergistic effects with multinuclear metal centers.[3b,8,9]

Herein, we report the successful development of a new single methylene-bridged tetraphosphine ligand, bis[(diphenylphosphinomethyl)phenylphosphino]methane (dpmppm), and demonstrate the construction of flexible tetragold(I) molecular chains which were further transformed to cyclic Au_6 and linear Au_8 structures. The Au_4 molecular units $[Au_4(\mu\text{-dpmppm})_2]^{4+}$ showed interesting luminescent properties and may have the potential to promote organic reactions with cooperative effects from multimetallic centers.[10]

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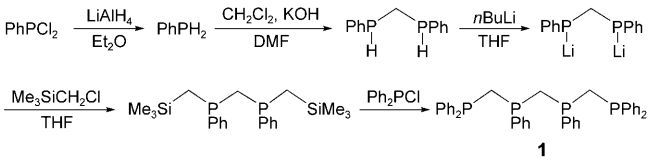
[**] This work was partly supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. Y.T. is grateful to the Japan Science Society for generous financial support (Sasakawa Scientific Research Grant) and to Nara Women's University for a grant for young female researchers.

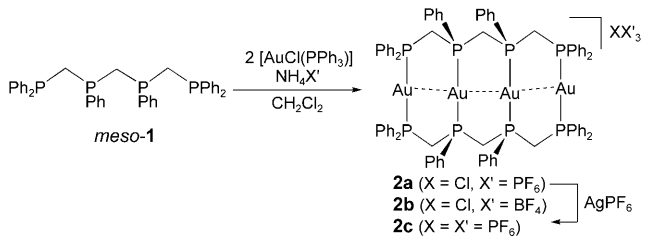
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200806012.

The reaction of bis(phenylphosphino)methane[8a,11] with *n*BuLi and Me_3SiCH_2Cl yielded bis[(trimethylsilylmethyl)-phenylphosphino]methane (tmsmppm). Addition of Ph_2PCl to tmsmppm afforded dpmppm (**1**) as a mixture of *meso*/*rac* diastereomers, the identity of which were confirmed by various spectroscopic methods (Scheme 1). After reprecipitation from acetone and washing with methanol, pure *meso*-dpmppm (*meso*-**1**) was obtained as a white powder.



Scheme 1. Synthesis of dpmppm (**1**).

When *meso*-**1** was treated with two equivalents of $[AuCl(PPh_3)]$[12] in the presence of NH_4X', linear tetragold(I) complexes $[Au_4(\mu\text{-dpmppm})_2]ClX'_3$ ($X' = PF_6$ (**2a**), BF_4 (**2b**)) were obtained in good yields (Scheme 2). Addition of



Scheme 2. Synthesis of tetragold(I) complexes with *meso*-dpmppm.

$AgPF_6$ to **2a** gave an anion-exchanged complex $[Au_4(\mu\text{-dpmppm})_2](PF_6)_4$ (**2c**). The ESI mass spectra of complexes **2a–c** in dichloromethane or acetone showed divalent parent peaks for $\{[Au_4(\mu\text{-dpmppm})_2]XX'\}^{2+}$ at m/z 1112.090 (**2a**: X = Cl, $X' = PF_6$), 1083.093 (**2b**: X = Cl, $X' = BF_4$), and 1167.083 (**2c**: $X = X' = PF_6$). These results demonstrated that tetragold(I) strings of complexes **2a–c** are stable in solution.

The structures of complexes **2a** and **2c** were determined by X-ray crystallography (Figure 1).[13] Complex **2a** consists of a bent Au_4 chain (Au-Au-Au 134.98(4), 137.37(3)°) bridged by two dpmppm ligands, which possesses a pseudo-C_2 axis that passes through the midpoint of Au2···Au3, these atoms have a further weak interaction with the Cl^- counterion (Figure 1 and 3a). The interatomic distances of 3.664(6) (Au1···Cl1), 3.132(6) (Au2···Cl1), 3.162(6) (Au3···Cl1), and

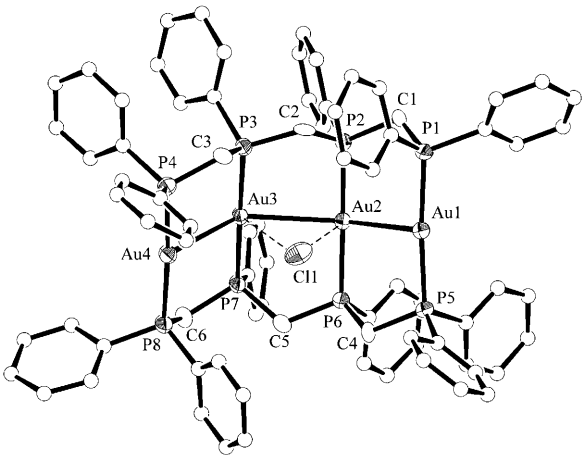
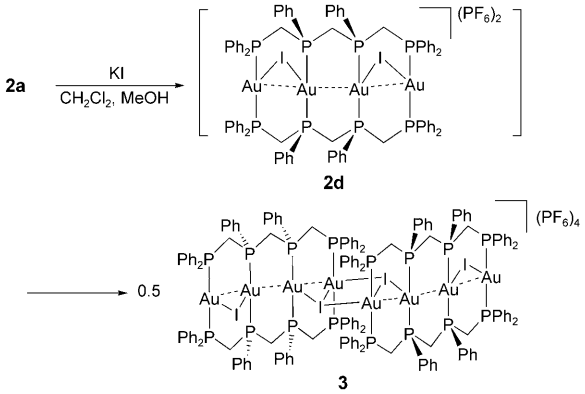


Figure 1. ORTEP plot of the complex cation of **2a**.

3.803(6) Å (Au4···Cl1) suggest the presence of electrostatic attractions between the inner two Au^{I} ions (Au2, Au3) and the Cl1 ion, as the sum of van der Waals radii (3.26 Å), and the outer gold atoms (Au1, Au4) are not within of the range of secondary interactions. The Au···Au separations (2.924(1)–2.953(1), average 2.942 Å) indicate the presence of an aurophilic interaction.[2] The *syn* arrangement of the two dpmppm ligands could accommodate linear Au_4 centers more naturally than the *anti* arrangement. Although the X-ray crystal structure of complex **2c** is essentially analagous with that of **2a**, the large Au-Au-Au angles (143.19(1), 163.89(1)°) of **2c** indicate that the degree of bending in the Au_4 structure of **2c** is remarkably reduced compared to that of **2a**. The large PF_6 ion fits well into the shallow pocket of **2c**, separations of Au1···F2 3.6392(8), Au2···F2 3.077(6), Au3···F1 3.081(6) Å, and Au4···F1 3.738(5) Å indicate the existence of attractive interactions between the inner Au atoms and the F atoms (Figure 3b). While the Au···Au distances are almost same as **2a**, the external Au···Au distances (2.9743(2), 2.9700(5) Å) in **2c** are slightly elongated compared to the central Au···Au distance (2.9595(3) Å). The distance between the outer Au ions is 8.271(1) Å, which is about 1.0 Å longer than that of **2a** (7.281(2) Å).

When complex **2a** was treated with 2.5 equivalents of KI in CH_2Cl_2/MeOH, orange crystals of the octagold(I) complex $[Au_8I_4(\mu\text{-dpmppm})_2](PF_6)_4$ (**3**) were obtained (Scheme 3). The complex cation of **3** has a linear octagold(I) core comprising two tetragold(I) units $[Au_4(\mu\text{-I})_2(\mu\text{-dpmppm})_2]^{2+}$



Scheme 3. Synthesis of octagold(I) complex **3**.

(**2d**) that are connected by two μ_3-iodide bridges (Figure 2).[13] The Au···Au separations (2.954(1)–3.0867(6) Å, average 3.022 Å) are slightly longer than those of **2a** and **2c**, and the Au–I distances are within the range 3.017(1)–3.232(2) Å (average 3.125 Å). Whereas the complex cation of **3** possesses a crystallographically imposed inversion center, the tetragold(I) fragment itself has a pseudo-C_2 axis on the midpoint of the two inner gold ions, as observed in **2a** and **2c**. In complexes **2a**, **2c**, and **3**, the average linearity of the Au-Au-Au angles in the Au_4 arrays increases from 136.17 (**2a**) and 153.54 (**2c**) to 161.55° (**3**), depending on the anion that interacts with the metal cores (Figure 3). Complex **3** might be an appropriate precursor for the construction of further expanded linear gold(I) arrangements.

The ESI mass spectrum of complex **3** in dichloromethane showed a divalent parent peak corresponding to $[Au_4I_2$-

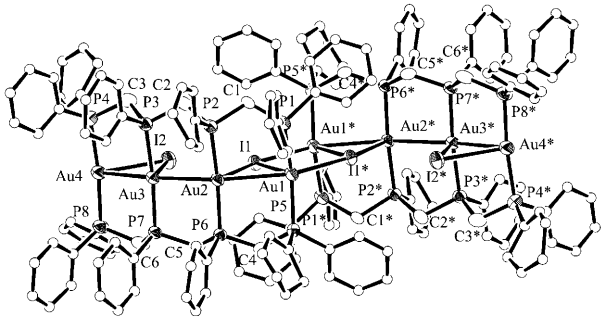


Figure 2. ORTEP plot of the complex cation of **3** (disordered phenyl groups were omitted for clarity).

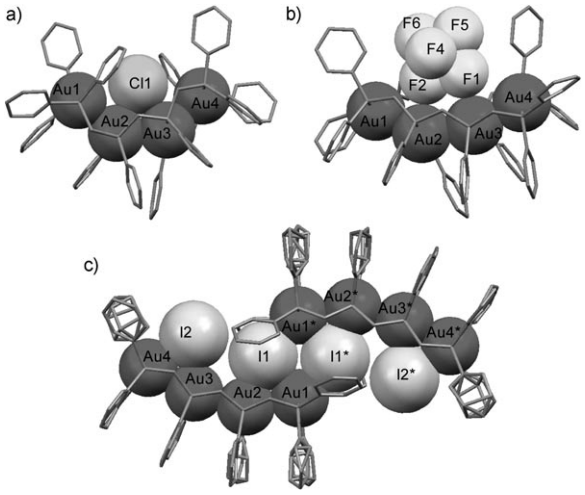


Figure 3. Perspective views showing the flexible interactions between the tetragold chains and anions in a) **2a**, b) **2c**, and c) **3**. For clarity, Au, I, Cl, and F ions are represented by van der Waal's radii and the dpmppm units by a stick model.

$(dpmppm)_2]^{2+}$ at m/z 1149.05. In the $^{31}P\{^1H\}$ NMR spectrum of **3**, two signals for the dpmppm ligands were observed at $\delta = 22.03$ (P_{in}) and 29.03 ppm (P_{out}). These spectral data suggest that complex **3** exists as the Au_4 unit $[Au_4(\mu\text{-}I)_2(\mu\text{-}dpmppm)_2](PF_6)_2$ (**2d**) in solution (Scheme 3). These chemical shifts are different from those of **2a** (P_{in} $\delta = 28.13$, P_{out} $\delta = 34.45$ ppm) and **2c** (P_{in} $\delta = 32.32$, P_{out} $\delta = 36.48$ ppm), with a larger upfield shift that arises from a stronger interaction with the halide ions. These results indicate that the interaction between the Au_4 units and the anions, which is observed in the X-ray crystal structures, is also retained in solution.

The UV/Vis absorption and emission spectra of **2a–c** and **3** are shown in Figure 4. A characteristic band was observed at 366 nm ($\varepsilon = 6.52 \times 10^4\ cm^{-1}M^{-1}$) together with a weak absorption at 293 nm ($\varepsilon = 2.29 \times 10^4\ cm^{-1}M^{-1}$) in the absorption

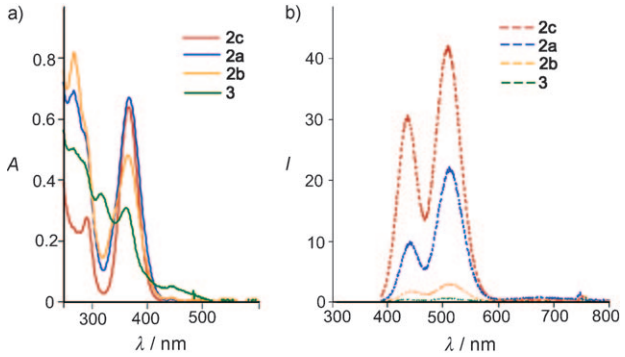


Figure 4. UV/Vis absorption (a) and emission (b) spectra of complexes **2a–c** and **3** in CH_2Cl_2 solution at room temperature.

spectrum of **2c**. On the basis of DFT calculations (B3LYP/LANL2DZ) on a model compound $[Au_4(\mu\text{-}H_2PCH_2P(H)CH_2P(H)CH_2PH_2)_2]^{4+}$ (**4**; the initial coordinates for optimization are derived from modification of the crystal structure of **2c**) and TD-DFT analysis, the lowest energy band is attributable to the $d_{\sigma^*\sigma^*\sigma^*} \rightarrow p_{\sigma\sigma\sigma}$ (HOMO→LUMO) transition ($\lambda = 290$ nm, f(oscillator strength) $= 0.46$; HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) and the second lowest energy band to the $d_{\sigma^*\sigma\sigma^*} \rightarrow p_{\sigma\sigma^*\sigma}$ (HOMO−1→LUMO+2) transition ($\lambda =$ 230 nm, $f = 0.12$; Figure 5), which are actually observed for **2c** at 366 and 293 nm, respectively. The former energy is appreciably lower than the $d_{\sigma^*} \rightarrow p_\sigma$ transition reported for digold(I) complexes with dppm and dcpm (ca. 270–300 nm).[5b,h] A solution of complex **2c** in CH_2Cl_2 is luminescent with emission band maxima at 509 and 437 nm, which are assigned to the emission from the $^3[d_{\sigma^*\sigma^*\sigma^*}p_{\sigma\sigma\sigma}]$ and $^3[d_{\sigma^*\sigma\sigma^*}p_{\sigma\sigma^*\sigma}]$ states respectively,[5g] based on the MO analysis. Interestingly, the emission signals of complexes **2a** and **2b** are appreciably quenched, presumably because of interaction of the Au_4 chain with the chloride ion. In complex **3**, the emission signals are completely quenched by the strong interaction with two iodide anions. These results revealed that the luminous flexible tetragold(I) unit supported by two dpmppm ligands $[Au_4(\mu\text{-}dpmppm)_2]^{4+}$ has potential to trap and detect halide ions in solution.

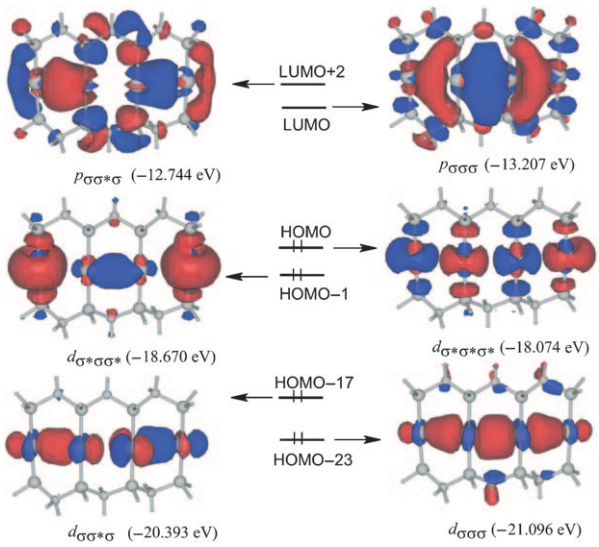


Figure 5. MO diagrams of the σ interactions between the four Au atoms, derived from DFT calculations on the model compound $[Au_4(\mu\text{-}H_2PCH_2P(H)CH_2P(H)CH_2PH_2)_2]^{4+}$ (**4**).

Reaction of complex **2a** with 1.2 equivalents of $NaAuCl_4$ afforded the cyclic hexagold(I) complex $[Au_6Cl_4(\mu\text{-}dpmppm)_2](PF_6)_2$ (**5a**). In the presence of NH_4Cl, colorless crystals of $[Au_6Cl_4(\mu\text{-}dpmppm)_2]Cl_2$ (**5b**) were also obtained. These complexes are insoluble in most organic solvents, which prevented detailed NMR spectroscopic analyses. However, the ESI mass spectra of **5a** and **5b** in acetone barely exhibited divalent parent peaks corresponding to $[Au_6Cl_4(dpmppm)_2]^{2+}$ at m/z 1290.072 (**5a**) and 1290.049 (**5b**), and confirmed their existence as the hexagold(I) unit in solution. The detailed structure of complex **5b** was determined by X-ray crystallography (Figure 6).[13] The complex cation of **5b** has a crystallographic inversion center and involves a cyclic Au_6 chain comprising six two-coordinated gold(I) ions bridged by two dpmppm ligands and ligated by four chloride ions. The Au1 atom is coordinated by the outer phosphorus atoms (P1 and

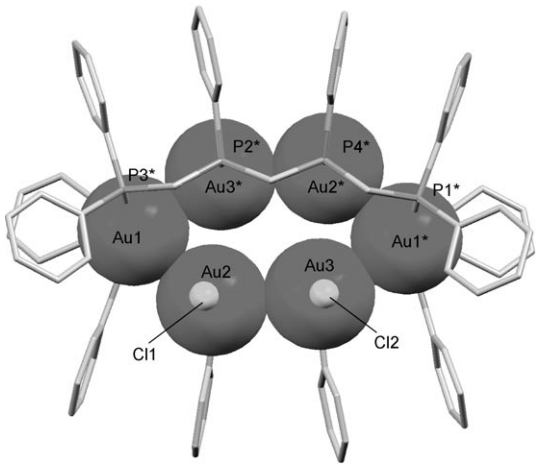


Figure 6. Perspective view of the complex cation of **5b**. For clarity, the Au ion is represented by its van der Waal's radius, Cl by a ball-and-stick model, and the dpmppm units by a stick model.

P3) of the dpmppm ligands (P-Au1-P 164.25(11)°) and the Au2 and Au3 atoms are ligated by a inner phosphorus atom (P2 or P4) and a chloride ion (P-Au-Cl 169.32(10), 175.17(13)°). The interatomic Au···Au distances in **5b** (3.1242(5), 3.0644(7), and 3.1726(7) Å) are longer than those of **2a**, **2c**, and **3**, and are still in the range of aurophilic interactions, as observed in gold(I) complexes with dpmp.[6] Whereas the hexagold(I) cycle of **5** is recognized as an expansion of the tetragold(I) cycle with dpmp ligands, $[Au_4Cl_2(\mu\text{-dpmp})_2]^{2+}$,[6f] the present results may imply the possibility of the bottom-up approach to the expanded linear and cyclic molecular structures formulated as $[\{Au_6Cl_4(\mu\text{-dpmppm})_2\}^{2+}]_n$. Furthermore, complex **5** could provide interesting organic reaction scaffolds as four reactive P-Au^I-Cl units are in proximity.[10]

In conclusion, we have synthesized the novel tetragold(I) chain complexes **2a–c** supported by a new linearly ordered tetraphosphine ligand. Complexes **2a–c** act as flexible molecular building blocks that lead to discrete linear octagold(I) (**3**) and cyclic hexagold(I) (**5**) complexes. The present results could provide useful bottom-up routes to nanostructured gold materials with constrained structures.

Received: December 10, 2008
Published online: February 9, 2009

Keywords: aurophilicity · coordination modes · gold · metal–metal interactions · P ligands

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[13] Crystal data for **2a** ($C_{78}H_{72}Au_4ClF_{18}P_{11}$): $M_r = 2515.43$ ($0.25 \times 0.20 \times 0.10$ nm); orthorhombic; *Pbca* (no. 61); $a = 21.878(5)$, $b = 28.997(6)$, $c = 31.616(7)$ Å; $V = 20057(8)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.666$ g cm^{-3}; $F(000) = 9600$; $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å, $\mu = 61.05$ cm^{-1}); $T = -120$ °C; a total of 22791 unique reflections ($R_{int} = 0.044$) were collected with a Rigaku/MSC Mercury CCD diffractometer ($6 < 2\theta < 55.0°$); $R1 = 0.090$ (12459 reflections,

$I > 2\sigma(I)$); $wR2 = 0.229$ for 1010 variables. Crystal data for **2c**·2$(CH_3)_2CO$·0.5Et_2O ($C_{86}H_{89}Au_4O_{2.5}F_{24}P_{12}$): $M_r = 2778.16$ ($0.45 \times 0.35 \times 0.20$ nm); triclinic; $P\bar{1}$ (no. 2); $a = 15.308(3)$, $b = 17.692(3)$, $c = 23.426(2)$ Å; $\alpha = 100.6360(4)$, $\beta = 95.612(2)$, $\gamma = 115.045(2)°$; $V = 5537.8(17)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.666$ g cm^{-3}; $F(000) = 2674$; $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å, $\mu = 55.54$ cm^{-1}); $T = -120$ °C; a total of 24653 unique reflections ($R_{int} = 0.027$) were collected with a Rigaku/MSC Mercury CCD diffractometer ($6 < 2\theta < 55.0°$); $R_1 = 0.048$ (20554 reflections, $I > 2\sigma(I)$); $wR_2 = 0.123$ for 1193 variables. Crystal data for **3** ($C_{78}H_{72}Au_4F_{12}I_2P_{10}$): $M_r = 2588.82$ ($0.35 \times 0.20 \times 0.20$ nm); triclinic; $P\bar{1}$ (no. 2); $a = 12.9914(2)$, $b = 18.0314(2)$, $c = 21.6093(5)$ Å; $\alpha = 78.120(6)$, $\beta = 79.548(7)$, $\gamma = 66.753(4)°$; $V = 4523.1(2)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.901$ g cm^{-3}; $F(000) = 2440$; $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å, $\mu = 74.13$ cm^{-1}); $T = -120$ °C; a total of 20124 unique reflections ($R_{int} = 0.112$) were collected with a Rigaku/MSC Mercury CCD diffractometer ($6 < 2\theta < 55.0°$); $R1 = 0.082$ (15507 reflections, $I > 2\sigma(I)$); $wR2 = 0.217$ for 1000 variables. Crystal data for **5b**·2$(CH_3)_2CO$ ($C_{84}H_{84}Au_6Cl_6O_2P_8$): $M_r = 2767.89$ ($0.35 \times 0.15 \times 0.10$ nm); triclinic, $P\bar{1}$ (no. 2); $a = 12.591(5)$, $b = 13.289(5)$, $c = 15.981(6)$ Å; $\alpha = 79.899(16)$, $\beta = 65.120(8)$, $\gamma = 86.242(16)°$; $V = 2388.1(16)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.925$ g cm^{-3}; $F(000) = 1300$; $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å, $\mu = 95.24$ cm^{-1}); $T = -120$ °C; a total of 10840 unique reflections ($R_{int} = 0.035$) were collected with Rigaku/MSC Mercury CCD diffractometer ($6 < 2\theta < 55.0°$); $R1 = 0.075$ (7960 reflections, $I > 2\sigma(I)$); $wR2 = 0.180$ for 539 variables. CCDC 712670 (**2a**), 712671 (**2c**), 712672 (**3**), and 712673 (**5b**) 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. ORTEP plots of complex **2c** and **5b** are given in the Supporting Information.