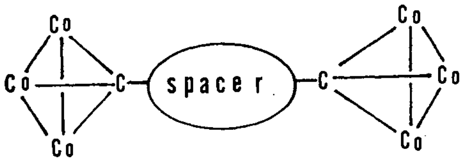
CHEMISTRY LETTERS, pp. 45-48, 1994.

Synthesis of Higher-nuclearity Clusters by Use of Small Cluster Units as Building Blocks. Syntheses and X-Ray Analyses of p-$[Co_3(CO)_9C]_2C_6H_4$ and $[CH_3CCo_3(CO)_8]_2(\mu\text{-dppfe})$

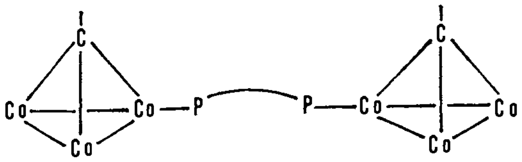
Satoru ONAKA,* Mayumi OTSUKA,† Atushi MIZUNO, Shigeru TAKAGI,
Katsuya SAKO, and Makoto OTOMO†
Department of Chemistry, †Department of Applied Chemistry, Nagoya
Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

Two units of $-CCo_3$ trinuclear cluster are systematically incorporated into various spacer molecules such as p-C_6H_4- and 1,1'-bis(diphenylphosphino)ferrocene, dppfe. X-Ray structure analysis has been made for p-$[Co_3(CO)_9C]_2$-C_6H_4 (**1**) and $[CH_3CCo_3(CO)_8]_2(\mu\text{-dppfe})$. Electronic interaction between two cluster units in **1** has been asserted by X-ray and absorption data.

Metal cluster chemistry is one of the most active research fields in organometallic and/or inorganic chemistry.[1] A continuing effort has been directed toward developing a better methodology for systematic synthesis of higher-nuclearity clusters in a fashion of molecular design, because the traditional methods such as pyrolysis and redox condensation of small clusters are sometimes elusive for predicting the products in advance.[1] Therefore, we have been interested in the construction of higher-nuclearity clusters and/or molecular superstructures by use of $-CCo_3(CO)_9$ units as building blocks, targetting to develop materials with exotic properties such as electronic, magnetic or optical characteristics. Our choice of this unit as a building block comes from the fact that the unit can employ a variety of substituents on the apical carbon, thus making it facile to incorporate the units into various kind of spacers (Type I). In addition, we have deemed that it is possible to link the cluster units at the basal cobalt atoms by use of diphosphine ligand such as dppfe(Type II), to which



Type I



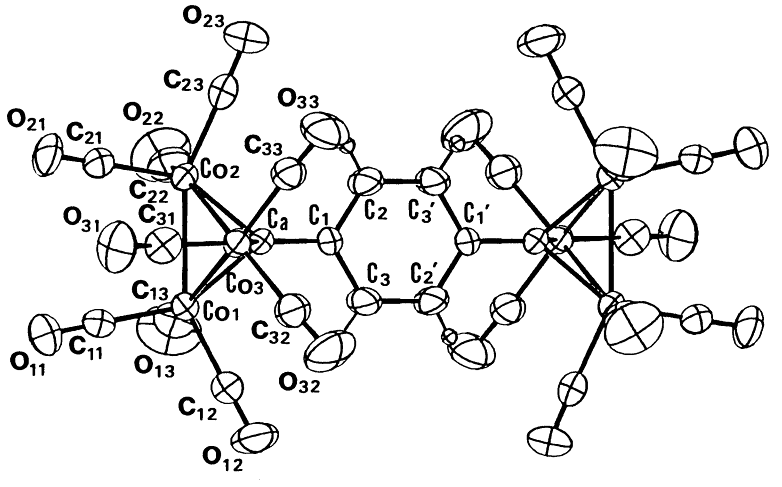
Type II

chemistry we have made a significant contribution recently.[2)] Here we report the syntheses of p-$[Co_3(CO)_9C]_2$-R (R = C_6H_4 (**1**) and $-C_6H_4-C_6H_4-$ (**2**)), $[CH_3CCo_3(CO)_8]_2$(μ-dppfe) (**3**), and $CH_3CCo_3(CO)_8$dppfe (**4**), X-ray analyses of **1** and **3**, and unusual behavior of **1**.

Thermal reaction of p-$(Cl_3C)_2C_6H_4$ with $Co_2(CO)_8$ in THF gave dark purple precipitates, which were washed with CH_2Cl_2 several times and were vacuum-dried to afford dark purple powder **1** with metallic luster in 10% yield. **1** was sparingly soluble in ordinary solvents at room temperature. X-ray analysis was made with a plate-like crystal which was grown-up from hot THF and has shown that **1** has two $-CCo_3(CO)_9$ units at para positions of the benzene ring (Fig. 1).[3)] **1** occupies the inversion center (the center of the benzene ring coincides with the center of inversion) and thus the view of the molecular packing in the cells looks as if they are stacked (figure is not shown).

2 was synthesized by reacting $BrCCo_3(CO)_9$ with p-$(LiC_6H_4)_2$ at low temperature in THF. The product was purified by silica-gel column with benzene as an eluent and recrystallization from toluene-benzene (1:1) gave dark-brown crystals of **2**,[4)] which are quite soluble in ordinary organic solvents in contrast to **1**.

A THF solution of $CH_3CCo_3(CO)_9$ was treated with a methanol solution of Me_3NO at room temperature. To this was added a THF solution of dppfe (0.5 equiv.) and the mixture was stirred at room temperature for 2 hr. After the solvent was distilled off at reduced pressure, the dark-brown residue was subjected to preparative TLC (silica gel, hexane:CH_2Cl_2 = 4:1) to afford **3** (dark-brown, yield 18%) and **4** (dark-brown, yield 11%).[4)] A plate-like

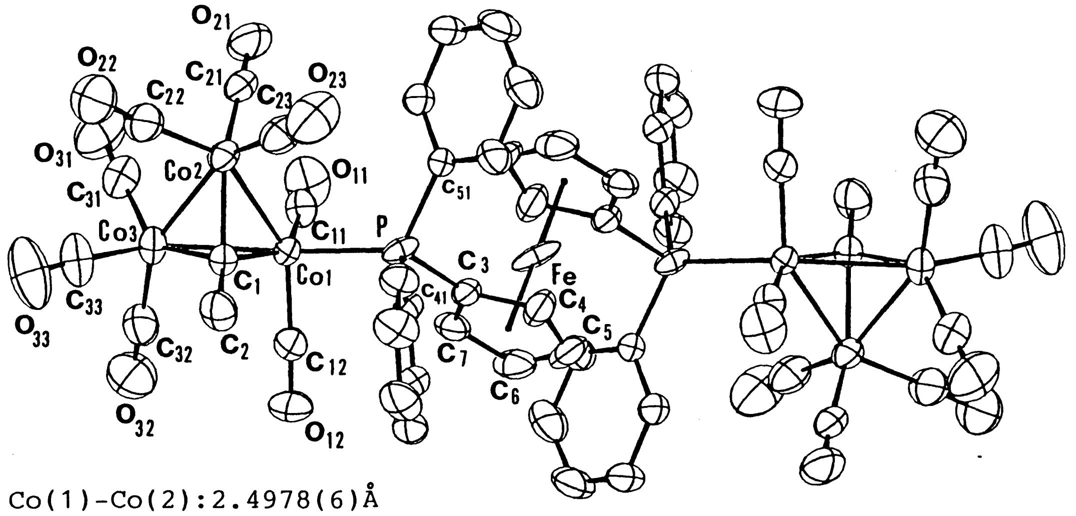


Co(1)-Co(2):2.474(1)Å
Co(2)-Co(3):2.470(1)
Co(3)-Co(1):2.471(1)
C(a)-C(1) :1.451(7)
C(1)-C(2) :1.356(8)
C(1)-C(3) :1.374(8)
C(2)-C(3) :1.38(1)
C(a)-Co(1) :1.914(5)
C(a)-Co(2) :1.916(5)
C(a)-Co(3) :1.919(5)
Co(1)-Co(2)-Co(3):59.97(3)°
Co(2)-Co(3)-Co(1):60.08(3)
Co(3)-Co(1)-Co(2):59.95(3)

Fig. 1. An ORTEP view of **1** and selected bond lengths and angles.

hexagon grown-up from hot hexane was used for X-ray analysis. The molecular structure of **3** is shown in Fig. 2; the iron atom in dppfe lies on a inversion center.5) The monodentate function of dppfe in **4** is confirmed by its ^{31}P-NMR spectrum, that is, two resonances are observed at δ -17.8 and 28.3, while **3** shows only one resonance at δ 41.8;in **4**, the former peak is characteristic to uncoordinated ^{31}P-nucleus and the latter peak characteristic to coordinated ^{31}P-nucleus, similar to $(MeCp)Mn(CO)_2$dppfe where dppfe functioned as a monodentate ligand.2)

Measurements of the electronic spectra for **1**, **2**, **3**, and **4** revealed unusual behavior of **1**, that is, the absorption around 500 nm, which is assigned to $\sigma(Co_3) \rightarrow a_2^*$ transition6) splits into two peaks (440 and 460 nm) with molar absorption coefficients which are about 10 times larger than those of **2**, **3**, **4**, and monoclusters, $RCCo_3(CO)_9$ (Fig. 3). The Co-Co distances and the C-C bond lengths of the spacer benzene ring in **1** are significantly shorter than those of 3 and $CH_3CCo_3(CO)_7$dppfe.2) These lines of evidence indicate strong interaction between two cluster units through the spacer moiety in **1**. This finding is important in regard to the possible electronic tuning via the choice of spacers and/or the substituents in spacer molecules.



Co(1)-Co(2):2.4978(6)Å
Co(2)-Co(3):2.4595(7)
Co(3)-Co(1):2.5059(8)
C(1)-C(2) :1.500(6)
Co(1)-P :2.240(1)
C(1)-Co(1) :1.888(4)
C(1)-Co(2) :1.906(4)

C(1)-Co(3) :1.932(3)Å
Co(1)-Co(2)-Co(3):60.72(2)°
Co(2)-Co(3)-Co(1):60.39(2)
Co(3)-Co(1)-Co(2):58.88(2)
P-Co(1)-Co(2) :103.99(3)
P-Co(1)-Co(3) :157.36(3)

Fig. 2. An ORTEP view of **3** and selected bond-lengths and angles.

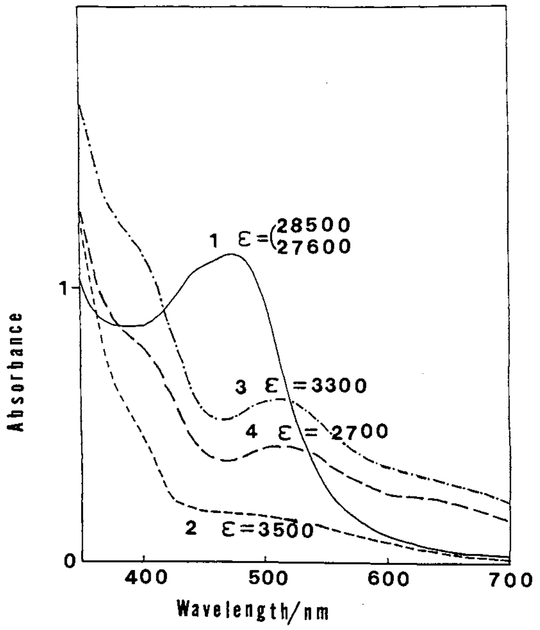


Fig. 3. Electronic spectra of 1, **2**, **3**, and **4** in CH_2Cl_2.

This work was supported by a Grant-in-Aid for Scientific Research (No. 03640516 and 05640627) from the Ministry of Education, Science and Culture, Japan.

References

1) D. F. Shriver, H. D. Kaesz, and R. D. Adams, "The Chemistry of Metal Cluster Complexes", VCH Publishers, New York 1990; J. P. Fackler, Jr., "Metal-Metal Bonds and Clusters in Chemistry and Catalysis", Plenum Press, New York 1990 and references therein.

2) S. Onaka, T. Moriya, S. Takagi, A. Mizuno, and H. Furuta, *Bull. Chem. Soc.Jpn.*, **65**, 1415 (1992); S. Onaka, H. Furuta, and S. Takagi, *Angew. Chem.,Int. Ed.*, **32**, 87 (1993)

3) Crystal Data of $p\text{-}[(CO)_9Co_3C]_2C_6H_4$:$C_{26}H_4Co_6O_{18}$, F.W.= 789.7, Triclinic, $P\bar{1}$, $a = 8.680(1)$, $b = 12.968(2)$, $c = 7.918(1)$ Å, $\alpha = 97.81(1)^\circ$, $\beta = 111.92(2)^\circ$, $\gamma = 78.89(1)^\circ$, $V = 809.6(3)$ Å^3, $Z = 1$, $D_c = 1.641$ gcm^{-3}, $R = 5.2\%$, $R_w = 3.4\%$, 2781 unique reflections with $|F_o| > 3\sigma(|F_o|)$.

4) Satisfactory results for elemental analysis and spectral measurements have been obtained for all these compounds.

5) Crystal Data of $[CH_3CCo_3(CO)_8]_2(\mu\text{-dppfe})$:$C_{54}H_{34}Co_6FeO_{16}P_2$, F.W.=1410.2, monoclinic, $P2_1/n$, $a = 16.585(2)$, $b = 11.624(1)$, $c = 15.556(2)$ Å, $\beta = 110.035(8)^\circ$, $Z = 2$, $V = 2817.6(5)$ Å^3, Dc = 1.663 gcm^{-3}, $R = 3.64\%$, $R_w = 6.65\%$, 4287 unique reflectons with $|F_o| > 3\sigma(|F_o|)$.

6) S. B. Colbran, B. H. Robinson, and J. Simpson, *Organometallics* , **2**, 943 (1983).

(Received September 28, 1993)