

**Synthesis of Higher-Nuclearity Clusters by Use of Small Cluster Units as Building Blocks:
Synthesis and X-Ray Structure Analysis of $[\text{ClCCo}_3(\text{CO})_8]_2(\mu\text{-dppe})$ and
 $[\text{ClCCo}_3(\text{CO})_7][\text{ClCCo}_3(\text{CO})_8](\mu\text{-TRIPHOS})$ (dppe=1,2-bis(diphenylphosphino)ethane;
TRIPHOS=bis(2-diphenylphosphinoethyl)phenylphosphine)¹**

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(Received January 10, 1995)

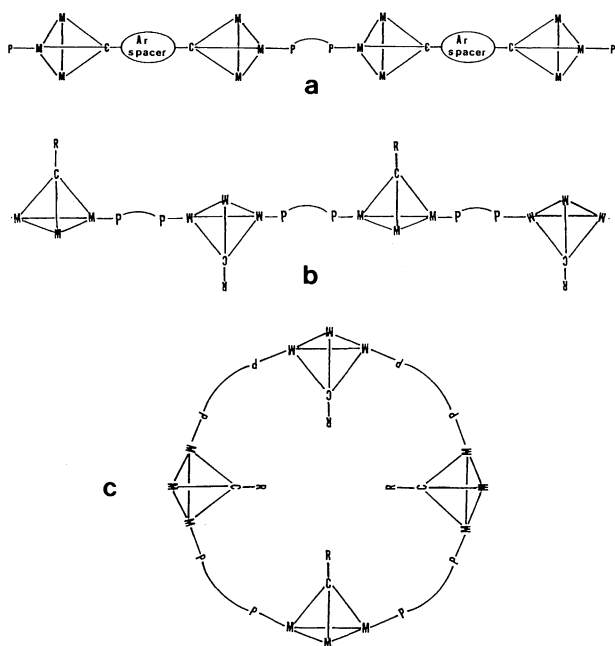
Two $\text{ClCCo}_3(\text{CO})_9$ units are, after treatment with Me_3NO , linked at basal cobalt atoms by dppe spacer to yield $[\text{ClCCo}_3(\text{CO})_8]_2(\mu\text{-dppe})$ and by TRIPHOS to yield $[\text{ClCCo}_3(\text{CO})_7][\text{ClCCo}_3(\text{CO})_8](\mu\text{-TRIPHOS})$; they are characterized by single crystal X-ray molecular structure analysis and two Cl atoms in the TRIPHOS derivative are found to be located in close proximity.

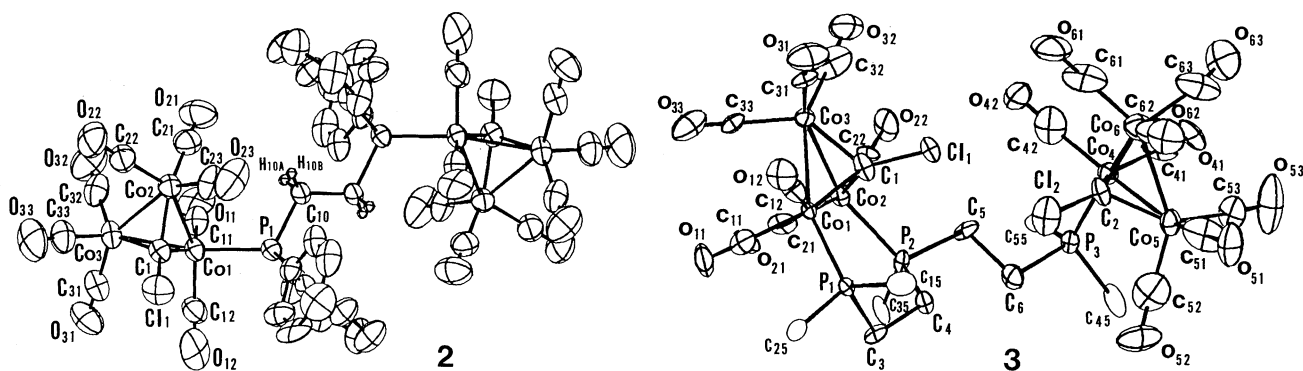
To construct higher-nuclearity clusters with well defined dimensions and structures provides a new field of chemistry with potential applications in areas including nanotechnology, molecular recognition, and catalyst.² We have been interested in the synthesis of higher-nuclearity clusters with purported arrangement of small cluster units of $\text{RCCo}_3(\text{CO})_9$ by the technique of molecular design (Scheme 1); linearly arranged supraclusters are expected to show interesting electronic properties such as quantum wire if their lengths are in the range of approximately 10 nm. In this regard, we have reported recently the synthesis of several prototype clusters in which two $\text{-CCo}_3(\text{CO})_9$ units are linked by benzene, biphenyl, and 1,1'-bis(diphenylphosphino)ferrocene, dppfe.³ In addition to application to molecular electronics, such supraclusters should have an opportunity to form a field for

excellent molecular recognition, because various kinds of substituents R can be introduced to such supraclusters⁴ and also it is possible to employ different functional groups of R in a single supracluster⁵; an appropriate combination of R should endow enzyme-like behavior for such clusters. The most efficient field for such molecular recognition among the proposed architectures in Scheme 1 is apparently formed by c which resembles calix arenes in the shape of central cavity. In order to synthesize such a cyclic and/or helical supraclusters, it is an essential stratagem to glean informations from prototype clusters on what kind of spacer will be able to form such an architecture. The previous paper has shown that dppfe is not a favorable spacer for such supraclusters, because the iron atom in dppfe lies on the inversion center for $[\text{MeCCo}_3(\text{CO})_8]_2(\mu\text{-dppfe})$,³ although dppfe has been shown to be a compliant ligand and to be able to change the angle required for tethering two metal sites in relevant multinuclear complexes.⁶ Therefore, we have examined dppe and TRIPHOS as a bridging spacer for construction of prototype clusters in which at least two $\text{RCCo}_3(\text{CO})_9$ units are incorporated. We have found that TRIPHOS is a favorable spacer for such an architecture. Here we report the synthesis and X-ray structure analysis for dppe- and TRIPHOS-bridged prototype clusters.

The cluster $[\text{ClCCo}_3(\text{CO})_8]_2(\mu\text{-dppe})$ (2) was easily prepared from $\text{ClCCo}_3(\text{CO})_9$ (1) and dppe. A THF solution (25 ml) of 1 (450 mg, 0.95 mmol) was treated under Ar with equimolar amount of Me_3NO which was dissolved in a minimum amount of methanol and THF. After CO evolution was ceased, the volume of the solution was reduced to half by vacuum distillation of the solvent. Then solid dppe (185 mg, 0.46 mmol) was added. The mixture was stirred at 25°C for 2 h. The solvent was vacuum-stripped to leave dark brown solid. This solid was subjected to silica-gel chromatography (Wako-gel C-200, eluted with hexane-benzene 4 : 1) to give brown cluster 2 in 19 % yield. The dark brown cluster $[\text{ClCCo}_3(\text{CO})_7][\text{ClCCo}_3(\text{CO})_8](\mu\text{-TRIPHOS})$ (3) was synthesized by adding 1/3 equivalent of solid TRIPHOS (170 mg, 0.31 mmol) to similarly prepared THF solution of 1 and by the same procedure of purification as above in 12 % yield.⁷ The molecular structures of these clusters are shown in Figure 1.⁸ 2 has the center of inversion at the midst of the $\text{-CH}_2\text{-CH}_2\text{-}$ bond in dppe. The main framework of the cluster 2, that is, Co-P-C-C-P-Co , composes a zigzag structure and two Cl atoms point to opposite directions along this chain. Therefore, if this prototype cluster is linked by dppe spacer further, the

Scheme 1.





Co₁-Co₂:2.509(1) Co₁-P₁:2.213(1) C₁-Co₂:1.883(2)
 Co₂-Co₃:2.473(1) Cl₁-C₁:1.744(2) C₁-Co₃:1.895(3)
 Co₃-Co₁:2.477(1) C₁-Co₁:1.860(2) P₁-C₁₀:1.843(2)
 Co₁-Co₂-Co₃:59.62(2) P₁-Co₁-Co₂:100.33(2)
 Co₂-Co₃-Co₁:60.92(2) P₁-Co₁-Co₃:158.36(2)
 Co₃-Co₁-Co₂:59.46(2) Co₁-P₁-C₁₀:113.7(1)

Co₁-Co₂:2.493(4) P₂-Co₂:2.197(7) Co₆-Co₄:2.482(5)
 Co₂-Co₃:2.496(4) Cl₁-C₁:1.76(3) P₃-Co₄:2.225(8)
 Co₃-Co₁:2.486(4) Co₄-Co₅:2.506(5) Cl₂-C₂:1.75(3)
 P₁-Co₁:2.192(7) Co₅-Co₆:2.496(5)
 P₁-Co₁-Co₃:157.4(3) P₃-Co₄-Co₆:153.6(2) Co₂-P₂-C₄:118.9(7)
 P₂-Co₂-Co₃:150.4(2) Co₁-P₁-C₃:116.8(7) Co₄-P₃-C₆:114.7(8)

Figure 1. Structures, bond-lengths(Å) and angles(°): 2 (left), 3 (right; Ph carbons but C₁ are omitted).

supracluster **b** in Scheme 1 will be constructed. The main framework of the cluster **3**, that is, Co-Co-P-C-C-P-Co composes a zigzag structure. However, two Cl atoms are located in close proximity; the distance between two Cl atoms is 3.29(1) Å. Thus, the prototype cluster **3** is a possible candidate to fabricate a cyclic supracluster **c** in Scheme 1 or a helical supracluster if further accumulation of this cluster on TRIPHOS is viable. Attempts along this line are now in progress in this laboratory.

UV and CV data for **2** and **3**⁹ do not show any anomaly which suggests interaction between two cluster units, the case of which has been demonstrated for p-[(OC)₉Co₃C]₂C₆H₄ recently.³ Thus, two cluster units, ClCCo₃(CO)_x are "insulated" from each other.

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

References and Notes

- This study was presented to the 16th International Conference on Organometallic Chemistry at University of Sussex, July 10-15, 1994.
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- For instance, we have succeeded to synthesize [MeCCo₃(CO)₈](μ-dppfe)[ClCCo₃(CO)₈]. S. Onaka, M. Otsuka, and S. Takagi, unpublished result.
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- 3** was eluted as the second brown band with hexane-benzene (4:1). The product obtained from the first brown band eluted with hexane-benzene 4:1 was ClCCo₃(CO)₇dppfe, determined by single crystal X-ray diffraction method.
- Crystal data: **2**, C₄₄H₂₄Cl₂Co₆O₁₆P₂, M = 1293.3, triclinic, space group P $\bar{1}$, a = 11.902(3), b = 12.126(3), c = 9.837(3) Å, α = 106.71(2)°, β = 110.26(3)°, γ = 86.55(2)°, V = 1274.4(6) Å³, λ = 0.71073 Å, Z = 1, D_c = 1.687 g cm⁻³, T = 297 K, μ (Mo-Kα) = 13.1 cm⁻¹. 3806 reflections with |F_o| > 3σ(|F_o|) (2θ_{max} = 50°) converged at R = 0.0273 and R_w = 0.0253.
- 3**, C₅₁H₃₃Cl₂Co₆O₁₅P₂, M = 1403.2, monoclinic, P2₁/a, a = 19.753(5), b = 19.179(7), c = 15.477(6) Å, β = 112.84(2)°, V = 5403(3) Å³, λ = 0.71073 Å, Z = 4, D_c = 1.724 g cm⁻³, T = 153.6 K, μ (Mo-Kα) = 12.22 cm⁻¹. 3450 reflections with |F_o| > 4σ(|F_o|) (2θ_{max} = 45°) converged at R = 0.0945 and R_w = 0.120.
- Selected spectroscopic data for: **2** ³¹P NMR (80.984 MHz, CDCl₃) δ 42.6, ¹H NMR (200 MHz, CDCl₃) δ 2.24 (s, 4H), 7.28 (s, 20H), IR, ν(CO) (KBr disk) 2088(vs), 2050(s), 2034(s), 2010(m), 1994(s), 1972(m) cm⁻¹, UV(cyclohexane) λ_{max} 405 nm (ε = 6900), 525 nm (ε = 3360). **3** ³¹P NMR (80.984 MHz, CDCl₃) δ 40.2, 42.7, ¹H NMR (200 MHz, CDCl₃) δ 2.12-2.32 (m, 8H), 7.35 (broad s; 25H), IR, ν(CO) (KBr disk) 2085(vs), 2060(s), 2035(m), 2020(s), 1980(m), 1920(m), UV(cyclohexane) λ_{max} 405 nm (ε = 11290), 520 nm (ε = 5740); ε/dm³ mol⁻¹ cm⁻¹.