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# Stepwise Synthesis of the Functionalized Metallatetrahedron $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7X$ ($X = Cl, Br, I$)

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In THF solution the dirhenium complex $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$ (**1**) reacts with an equimolar amount of LiPh at −100 °C to afford after warming up to room temperature within 1 h the salt $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(C(Ph)O)(CO)_7]$ (**Li[2]**). Through cation exchange of $Li^+$ against $PPh_4^+$, **Li[2]** gives the airstable solid **PPh$_4$[2]** in 86% yield. The selectivity of the LiPh attack at one of the four axial carbonyls in **1** was proved by the chiral shift reagent $Eu(hfac)_3$ which was dissolved in a $CDCl_3$ solution of **PPh$_4$[2]**. The $^1H$ and $^{31}P$ NMR spectra show the diastereomeric resolution of the respective peaks in an integral ratio of 1:1 e.g. $\Delta\delta(\mu\text{-}P)$ 0.43. The anion **[2$^-$]** generates with 2 equiv of $XAuPPh_3$ ($X = Cl, Br, I$) in THF at room temperature within 15 min under release of the leaving group PhCHO the yellow cluster complexes $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7X$ (**4a**−**c**). Their precursor complex anions $[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7X]^-$ (**3a**−**c**) are obtained from **1** and an equimolar amount of $XAuPPh_3$ or from the deauration by treatment of **4a** ($X = Cl$) with 1 equiv of LiPh via a transmetalation reaction. Such anions are isolable as salts, **N(PPh$_3$)$_2$[3a−c]**. All new cluster complexes are identified by means of $^1H$ NMR, $^{31}P$ NMR and $\nu(CO)$ IR spectroscopic measurements, **Li[2]** and **4a** ($X = Cl$) additionally by means of X-ray single-crystal structure analyses. **Li[2]** crystallizes triclinic, space group $P\bar{1}$, $Z = 2$, $a = 10.536(2)$ Å, $b = 11.433(2)$ Å, $c = 19.125(3)$ Å, $\alpha = 98.01(1)°$, $\beta = 89.94(1)°$, and $\gamma = 112.22(1)°$; **4a** crystallizes monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 18.615(5)$ Å, $b = 13.606(2)$ Å, $c = 24.223(6)$ Å, and $\beta = 105.14(2)°$. The molecular structure of **Li[2]** shows a $\mu$-H-, $\mu$-P-bridged Re−Re bond of 3.1667(7) Å, the one of **4a** a tetrahedrally shaped $Re_2Au_2$ core with a $\mu$-P-bridged Re−Re edge of 3.2680(10) Å.

## Introduction

Previously, we described the deprotonation of $\mu$-hydrido-/$\mu$-phosphido-bridged dinuclear transition metal complexes $M_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_8$ ($M = Mn, Re$; $R = R' =$ alkyl, aryl; $R' = H$) with nonnucleophilic nitrogen bases to either as solid isolable or in solution identifiable anions. Such anions can also be trapped with cations like $PR_3Au^+$ to generate neutral heterometallic cluster complexes with structurally different $M_2Au_n$ ($n = 1,2$) cores.[1−3] In addition we used nucleophilic lithium organyls in excess starting from the diorganophosphido-bridged derivates. In this case, the unidentified anionic intermediates provided, with 2 equiv of the scavenger $PPh_3Au^+$, mainly triangular and tetrahedral cluster complexes of the types $M_2(\mu\text{-}AuPR_3)(\mu\text{-}PR_2)(CO)_8$ and $M_2(\mu\text{-}C(R)O)(\mu\text{-}PR_2)(CO)_6(AuPPh_3)_2$. On the basis of such findings a mechanistic pathway was proposed, although the actual reaction steps of the nucleophile LiR remained obscure.[4,5] With the priority on mechanistic studies of these complex transformations we now report on the reaction between $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$ (**1**) and LiPh (molar ratio 1:1) to give the racemic salt $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)C(Ph)O)(CO)_7]$ (**Li[2]**) and its consecutive reaction with $ClAuPPh_3$ to give a tetrahedral cluster complex with a $Re_2Au_2$ core accompanied by the unexpected release of PhCHO. The present work is a continuation of our efforts to prepare small heterometallic cluster complexes in a directed synthesis. This is not only to gain information about the nature of heterometallic bonding but also because these compounds reveal special reactivities due to the cooperative effects of their metal atoms.[6] Particular attention has been drawn to the optical properties of a chiral heterometallic framework[7,8] and to catalysis.[6,9,10] Moreover, these studies could enable the future syntheses of a chiral tetrahedral framework with four different metal atoms.[11]

## Experimental Section

Infrared spectra were recorded on a Nicolet P510 FT IR spectrometer. Proton NMR and phosphorus-31 NMR spectra were recorded on a Bruker AMX 300 multinuclear pulsed Fourier transform spectrometer at 300 and 121.5 MHz, respectively, using internal tetramethylsilane and external 85% phosphoric acid, respectively, as a reference. Chemical shifts $\delta$ are given in ppm downfield from the reference. All reactions were carried out under an argon atmosphere. Tetrahydrofuran, dichloromethane, hexane, and methanol were dried according to the literature methods, distilled and stored in the presence of argon. The complexes $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$[12] and $XAuPPh_3$ ($X = Cl, Br, I$)[14,15]

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(1) Haupt, H.-J.; Schwefer, M.; Flörke, U. *Inorg. Chem.* **1995**, *34*, 292.

(2) Haupt, H.-J.; Schwefer, M.; Egold, H.; Flörke, U. *Inorg. Chem.* **1995**, *34*, 5461.

(3) Haupt, H.-J.; Schwefer, M.; Flörke, U. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1098.

(4) Haupt, H.-J.; Heinekamp, C.; Flörke, U. *Inorg. Chem.* **1990**, *29*, 2955.

(5) Haupt, H.-J.; Heinekamp, C.; Flörke,U.; Jüptner, U. *Z. Anorg. Allg. Chem.* **1992**, *608*, 100.

(6) Gladfelter, W. L.; Rosselet, K. J. In *Cluster Complexes as Homogeneous Catalysts and Catalyst Precursor in Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams; R. D., Eds.; VCH Publisher Inc.: New York, 1990.

(7) Richter, F.; Vahrenkamp, H. *Angew. Chem.* **1980**, *92*, 66; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 65.

(8) Vahrenkamp, H. *J. Organomet. Chem.* **1989**, *370*, 65.

(9) Darjusch, M.; Schacht, H.-T.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1989**, *122*, 2245.

(10) Schacht, H.-T.; Vahrenkamp, H. *Chem. Ber.* **1989**, *122*, 2253.

(11) Richter, F.; Beurich, H.; Müller, M.; Gärtner, N.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 3774.

(12) Haupt, H.-J.; Merla, A.; Flörke, U. *Z. Anorg. Allg. Chem.* **1994**, *620*, 999.

(13) Haupt, H.-J.; Gohlke, C. Unpublished results.

(14) Brauer, G. *Handbuch der Präparative Anorgische Chemie*, 3. Aufl.; F. Enke Verlag: Stuttgart, Germany 1981.

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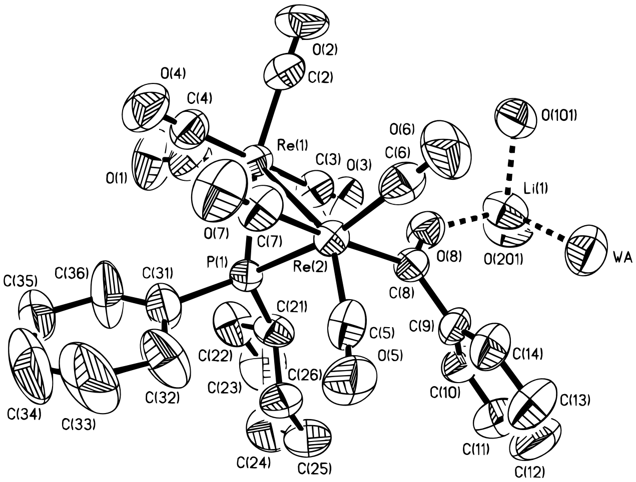

**Figure 1.** Molecular structure of **Li[2]**. Hydrogen atoms were omitted. O(101) and O(102) denote the THF oxygen atoms; Wa denotes the solvent water oxygen atom. ORTEP plot showing 50% probability for thermal ellipsoids.

were prepared according to known synthetic routes. Elemental analyses were performed for all new compounds prepared except for the lithium salts.

**Preparation of $[M]^+[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(C(Ph)O)(CO)_7]^-$ (M[2] = [Li][2]) or [PPh$_4$][2]).** A solution of $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$ (**1**) (150 mg, 0,189 mmol) in about 5 mL of THF was cooled down to −100 °C and then treated with 95 $\mu$L of a 2 M solution of LiPh in cyclohexane/ether. When this was warmed up to room temperature within 1 h, the color of the solution turned yellow and a $^{31}$P-NMR spectrum of the reaction liquid indicated the quantitative formation of **[2$^-$]**. The solvent was removed under reduced pressure and the resulting residue taken up in 3 mL of methanol. After 100 mg of $[PPh_4]Br$ (0.238 mmol) was added, a few milliliters of water (saturated with Ar) were dropped in until no more precipitation occurred. The precipitate was filtered off, washed with *n*-hexane, and vacuum dried. Yield: 197 mg (86%) of **[PPh$_4$][2]**. Crystallization from $CHCl_3$ solution in the presence of *n*-pentane (vapor diffusion method) led to yellow crystals of **[PPh$_4$]-[2]**. Crystals of the pure Li compound **Li[2]** (Figure 1) were obtained by vaporizing the THF solution in the presence of *n*-pentane.

**Li[2]**. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2078 m, 1993 vs, 1977 m, 1968 sh, 1929 m, 1896 s, 1885 s. $^1$H NMR (THF-$d_8$): $\delta$ −13.11 (d; $^2J_{PH}$ = 8.5 Hz; 1H, $\mu$-H); 1.10−2.23 (m; 22H; Cy); 7.05−7.60 (m; 5H; Ph). $^{31}$P NMR (THF): $\delta$ 63.4 (s; 1P, $\mu$-P).

**[PPh$_4$][2]**. Anal. Calcd: C, 49.58; H, 3.99. Found: C, 49.62; H, 4.06. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2072 s, 1987 s, 1973 m, 1956 m, 1919 vs, 1883 vs, 1871 vs. $^1$H NMR ($CDCl_3$): $\delta$ −13.08 (d; $^2J_{PH}$ = 10 Hz; 1H, $\mu$-H); 1.12−2.15 (m; 22H; Cy); 7.09−7.92 (m; 25H; Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 23.0 (s; 1P, $[PPh_4]^+$); 72.3 (s; 1P, $\mu$-P).

NMR spectra with shift reagent (15 mg of **PPh$_4$[2]** and 20 mg of $Eu(hfac)_3$ in 1 mL $CDCl_3$) were obtained. $^1$H NMR: $\delta$ −10.99 (d; $^2J_{PH}$ = 10 Hz; 1H, $\mu$-H); −11.33 (d; $^2J_{PH}$ = 10 Hz; 1H, $\mu$-H), integral ratio 1:1. $^{31}$P NMR: $\delta$ 23.78 (s; 1P, $[PPh_4]^+$); 70.46 (s; 1P, $\mu$-P); 70.90 (s; 1P, $\mu$-P), integral ratio 1:1.

**Preparation of $[M]^+[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7X]^-$ ([M][3a] = [Li][3a], [N(PPh$_3$)$_2$][3a]; [M][3b] = [Li][3b], [N(PPh$_3$)$_2$][3b]; [M]-[3c] = [Li][3c], [N(PPh$_3$)$_2$][3c]; in 3a$^-$, X = Cl, in 3b$^-$, X = Br, and in 3c$^-$, X = I).** A THF solution (3 mL) of 0.189 mmol of $XAuPPh_3$ (X = Cl; 93 mg; X = Br, 102 mg; X = I, 586 mg) was added dropwise to a THF solution (5 mL) of **Li[2]** (0.189 mmol), which was prepared as described above. After this mixture was stirred at room temperature for 15 min, IR and $^{31}$P NMR spectra recorded showed the quantitative formation of **[3a$^-$]**, **[3b$^-$]**, and **[3c$^-$]**, respectively (see data below). For isolation of the complex anions 92 mg of $[N(PPh_3)_2]Cl$ (0.189 mmol) was added. The solution was then evaporated in vacuum and the resulting residue redissolved in $CH_2Cl_2$. The insoluble LiCl remained as white residue which was filtered off, and the filtrate was again evaporated to leave a yellow product, which was washed three times with a cold mixture of *n*-hexane and $CH_2Cl_2$ (1/5). In this way **(N(PPh$_3$)$_2$[3a], X = Cl)**, **(N(PPh$_3$)$_2$[3b], X = Br)** and **(N(PPh$_3$)$_2$[3c], X = I)**, respectively, were obtained as amorphous yellow powders in 70% yield.

**Li[3a].** $\nu$(CO) IR (THF) [cm$^{-1}$]: 2047 m, 1975 s, 1956 vs, 1939 s, 1902 vs, 1879 vs, 1855 vs (1705). $^{31}$P NMR (THF): $\delta$ 85.1 (d; $^3J_{PP}$ = 9 Hz; 1P, PPh$_3$); 158.1 (d; $^3J_{PP}$ = 9 Hz; 1P, $\mu$-P).

**Li[3b].** $\nu$(CO) IR (THF) [cm$^{-1}$]: 2047 m, 1973 s, 1958 vs, 1931 s, 1894 vs, 1881 s, 1854 vs (1705). $^{31}$P NMR (THF): $\delta$ 84.4 (d; $^3J_{PP}$ = 10 Hz; 1P, PPh$_3$); 158.1 (d; $^3J_{PP}$ = 10 Hz; 1P, $\mu$-P).

**Li[3c].** $\nu$(CO) IR (THF) [cm$^{-1}$]: 2048 m, 1973 m, 1954 s, 1937 vs, 1900 vs, 1883 s, 1860 vs (1705). $^{31}$P NMR (THF): $\delta$ 83.8 (d; $^3J_{PP}$ = 9 Hz; 1P, PPh$_3$); 145.4 (d; $^3J_{PP}$ = 9 Hz; 1P, $\mu$-P).

**[N(PPh$_3$)$_2$][3a].** Anal. Calcd: C, 48.74; H, 3.75; N, 0.78. Found: C, 48.56; H, 3.92; N, 0.82. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2044 m, 1975 m, 1954 m, 1931 s, 1892 vs, 1879 s, 1852 vs. $^1$H NMR ($CDCl_3$): $\delta$ 1.1−2.5 (m; 22H; Cy); 7.1−7.7 (m; 45H; Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 21.7 (s; 2P, $[(PPh_3)_2N]^+$); 84.7 (d; $^3J_{PP}$ = 10 Hz; 1P, PPh$_3$(Au)); 158.7 (d; $^3J_{PP}$ = 10 Hz; 1P, $\mu$-P).

**[N(PPh$_3$)$_2$][3b].** Anal. Calcd: C, 47.56; H, 3.66; N, 0.76. Found: C, 47.41; H, 3.81; N, 0.81. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2044 m, 1975 m, 1956 m, 1930 s, 1894 vs, 1880 sh (s), 1853 s. $^1$H NMR ($CDCl_3$): $\delta$ 1.2−2.5 (m; 22H; Cy); 7.2−7.8 (m; 45H; Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 21.7 (s; 2P, $[(PPh_3)_2N]^+$); 84.5 (d; $^3J_{PP}$ = 10 Hz; 1P, PPh$_3$(Au)); 154.0 (d; $^3J_{PP}$ = 10 Hz; 1P, $\mu$-P).

**[N(PPh$_3$)$_2$][3c].** Anal. Calcd: C, 46.38; H, 3.57; N, 0.74. Found: C, 46.43; H, 3.59; N, 0.78. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2044 m, 1975 m, 1952 m, 1930 s, 1894 vs, 1882 sh(s), 1857 s. $^1$H NMR ($CDCl_3$): $\delta$ 1.2−2.5 (m; 22H; Cy); 7.2−7.8 (m; 45H; Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 21.7 (s; 2P, $[(PPh_3)_2N]^+$); 83.7 (d; $^3J_{PP}$ = 11 Hz; 1P, PPh$_3$(Au)); 146.0 (d; $^3J_{PP}$ = 11 Hz; 1P, $\mu$-P).

**Preparation of $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7X$ (4a, X = Cl; 4b, X = Br; 4c, X = I).** A 0.189 mmol sample of $XAuPPh_3$ (94 mg for X = Cl, 102 mg for X = Br, 111 mg for X = I) was added to a THF solution of **Li[3a]**, which was prepared as described above. After 15 min of stirring, the solvent was removed under reduced pressure. Subsequently, the residue obtained was taken up in 5 mL of $CH_2Cl_2$ and purified by TLC (1 mm gypsum/silica gel, Merck, with eluent *n*-hexane/$CH_2Cl_2$ (1:1)). Crystallization of the products in toluene/*n*-pentane led to deep yellow needles of $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7X$ (**4a**−**c**) in an almost quantitative yield.

**4a.** Anal. Calcd: C, 38.41; H, 3.05. Found: C, 38.43; H, 3.11. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2056 s, 1997 vs, 1975 m, 1958 m, 1933 vs, 1921 s, 1875 s. $^1$H NMR ($CDCl_3$): $\delta$ 1.2−2.5 (m; 22H; Cy); 7.2−7.6 (m; 30H; Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 60.4 (d; $^3J_{PP}$ = 18 Hz; 1P, PPh$_3$); 64.4 (d; $^3J_{PP}$ = 18 Hz; 1P, PPh$_3$); 132.9 (s; 1P, $\mu$-P).

**4b.** Anal. Calcd: C, 37.45; H, 2.97. Found: C, 37.49; H, 3.03. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2056 s, 1996 vs, 1971 m, 1959 m, 1934 vs, 1921 s, 1876 s. $^1$H NMR ($CDCl_3$): $\delta$ 1.2−2.5 (m; 22H; Cy); 7.2−7.6 (m; 30H; Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 62.7 (d; $^3J_{PP}$ = 15 Hz; 1P, PPh$_3$); 64.9 (d; $^3J_{PP}$ = 15 Hz; 1P, PPh$_3$); 125.0 (s; 1P, $\mu$-P).

**4c.** Anal. Calcd: C, 36.47; H, 2.89. Found: C, 36.51; H, 2.99. $\nu$(CO) IR (THF) [cm$^{-1}$]: 2054 s, 1996 vs, 1969 m, 1959 m, 1932 vs, 1921 sh(s), 1882 s. $^1$H NMR ($CDCl_3$): $\delta$ 1.2−2.4 (m; 22H; Cy); 7.2−7.6 (m; 30H; Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 66.0 (d; $^3J_{PP}$ = 10 Hz; 1P, PPh$_3$); 70.3 (d; $^3J_{PP}$ = 10 Hz; 1P, PPh$_3$); 114.6 (s; 1P, $\mu$-P).

**Structure Determination of Li[2] (Figure 1).** Lattice parameters were refined from 30 reflections $15 \le 2\theta \le 30°$. Data were collected on a Siemens R3m diffractometer, with an $\omega/2\theta$ scan, $3 \le 2\theta \le 55°$, and 9800 intensities; three standards recorded every 400 showed 7% decrease, and intensities were corrected accordingly, by *Lp* and empirical absorption corrections ($\psi$ -scans); after merging ($R_{int}$ = 0.031) there were 9535 unique intensities. The structure was solved by direct and conventional Fourier methods, with full-matrix least-squares refinement based on $F^2$ and 472 parameters, with all but H-atoms refined anisotropically, H atoms were fixed at idealized positions with “riding” model, and the $\mu$-H atom position could not be determined but was ascertained from $^1$H NMR measurements. One solvent water molecule and two solvent THF molecules per asymmetric unit. Further informa-

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(15) McAuliffe, C. A.; Parish, R. V.; Randall, P. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1730.

**Table 1.** Crystallographic Data for **Li[2]** and **4a**[a]

| | **Li[2]** | **4a** |
|---|---|---|
| formula | Li[$C_{34}H_{46}O_{11}PRe_2$]·2THF·$H_2O$ | $Au_2C_{55}H_{52}ClO_7P_3Re$·$CH_2Cl_2$ |
| mol wt | 1041.0 | 1803.1 |
| cryst size, mm | 0.15 × 0.48 × 0.55 | 0.10 × 0.11 × 0.58 |
| space group (No.) | $P\bar{1}$ (2) | $P2_1/c$ (14) |
| $a$, Å | 10.536(2) | 18.615(5) |
| $b$, Å | 11.433(2) | 13.606(2) |
| $c$, Å | 19.125(3) | 24.223(6) |
| α, deg | 98.01(1) | |
| $\beta$, deg | 89.94(1) | 105.14(2) |
| $\gamma$, deg | 112.22(1) | |
| $V$, Å$^3$ | 2108.5(6) | 5992(2) |
| $Z$ | 2 | 4 |
| $D_{\mathrm{calc}}$, g/cm$^3$ | 1.640 | 2.022 |
| $F$(000) | 1012 | 3400 |
| $\mu$, mm$^{-1}$ | 5.823 | 9.278 |
| transm coeff | 0.171 / 0.597 | 0.464 / 0.527 |
| R1; wR2 (all data) | 0.053; 0.170 | 0.074; 0.159 |

[a] For all structures, Mo Kα radiation was used at $T = 296$ K. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = (\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2))^{1/2}$.

tion is given in Table 1. Scattering factors, structure solution, and refinement used SHELXTL V5.[16]

**Structure Determination of 4a (Figure 2).** Lattice parameters were refined from 30 reflections, $14 \leq 2\theta \leq 30°$, with $\omega/2\theta$-scan, $3 \leq 2\theta \leq 55°$, and 13991 intensities. Three standards recorded as before showed 10% decrease; intensities were corrected accordingly. Corrections and structure solution were as before. A total of 13666 independent reflections were observed ($R_{\mathrm{int}} = 0.062$). Refinement was based on $F^2$ and 587 parameters, phenyl groups were treated as rigid bodies (C-C 1.395 Å), all but H-atoms refined anisotropically, and H atoms and programs were as before.

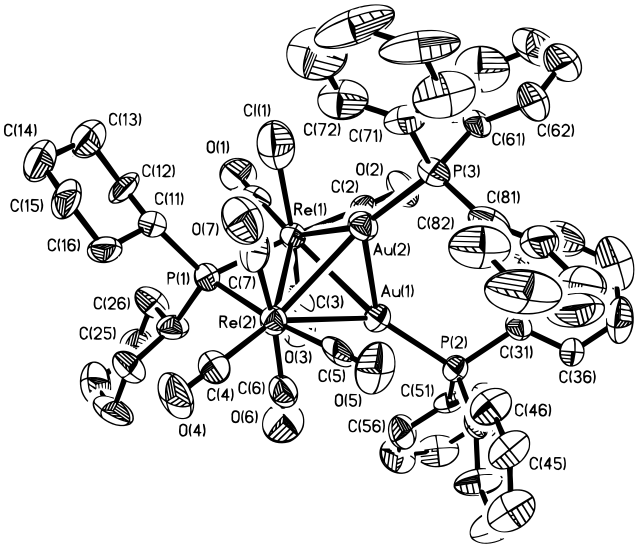

**Figure 2.** Molecular structure of **4a**. Hydrogen atoms were omitted. The ORTEP plot shows 50% probability for thermal ellipsoids.

## Results and Discussion

The reaction of **1** with nonnucleophilic nitrogen bases like DBU leads to a selective deprotonation of the $\mu$-H functional group, yielding the anionic species [$Re_2$($\mu$-$PCy_2$)$(CO)_8$]$^-$.[12] When $Re_2$($\mu$-H)($\mu$-$PPh_2$)$(CO)_8$ was treated with strong nucleophilic bases like LiR (R = Me, Bu, Ph) in a 2-fold excess, an alkylation of the carbonyl groups occurred along with elimination of the $\mu$-H atom. For example for LiPh, this was shown by scavenging the resulting anion with 2 equiv of $ClAuPPh_3$ and an X-ray crystallographic determination of the main product ($\mu$-$PPh_2$)($\mu$-C(Ph)O)$(CO)_6Re_2(AuPPh_3)_2$. A mechanistic pathway of its formation was proposed, proceeding from a deprotonation of the $\mu$-H atom as the initial step followed by a nucleophilic attack of LiPh at a carbonyl ligand with formation of a monodentate phenyl acyl group.[4] Recently, our attempts to prove such a reaction pattern between **1** and LiPh in a molar ratio 1:1 and 1:2 were directed toward the separation of the corresponding presupposed anions. Already $^1$H NMR measurements of such reaction solutions with a NMR spectrometer of higher specification than used earlier led us surprisingly to recognize that in both cases the $\mu$-H ligand in **1** remained. LiPh converted selectively one of the two axial carbonyl groups arranged at each of both Re atoms in **1** to a monovalent phenyl acyl ligand and did not allow a direct deprotonation of the $\mu$-H ligand. In the following, we report on the preparation and chemical properties of the monoanion **[2$^-$]**, while the treatement of the dianion which delivered the known phenylacyl-bridged cluster $Re_2$($\mu$-C(Ph)O)($\mu$-$PR_2$)$(CO)_6(AuPPh_3)_2$ (R = Ph, Cy)[4,13] will be given in a further paper.

**Reaction of $Re_2$($\mu$-H)($\mu$-$PCy_2$)$(CO)_8$ (1) with LiPh.** A solution of **1** in THF ($^{31}$P NMR: $\delta$ 63.0 (s; 1P, $\mu$-P)) was treated with an equimolar amount of LiPh at a temperature of −100 °C. When this was warmed up to room temperature within 1 h, the color of the solution turned yellow. A $^{31}$P NMR spectrum of the reaction liquid indicated the quantitative formation of a new compound ($^{31}$P NMR: $\delta$ 63.4 (s; 1P, $\mu$-P)). Evaporating THF in the presence of *n*-pentane yielded some single crystals, which were identified as Li[$Re_2$($\mu$-H)($\mu$-$PCy_2$)(C(Ph)O)$(CO)_7$] (**Li[2]**) by single crystal X-ray analysis (Figure 1) as well as by $^{31}$P/$^1$H NMR and IR spectroscopic data. The existence of the $\mu$-H atom in **[2$^-$]** was proved by an $^1$H NMR spectrum (THF-$d_8$), which showed a doublet ($^2J_{PH} = 8.5$ Hz) at −13.11 ppm compared to −15.01 (d, $^2J_{PH} = 5.9$ Hz; 1H, $\mu$-H) in **1**.[12] As expected, the IR spectrum of **[2$^-$]** displays 7 vibrational bands due to the 7 CO ligands of this chiral complex anion. It is evident from the structural features of **Li[2]**, that **1** was selectively attacked at one of its axially bonded four carbonyl ligands forming an acyl ligand (Figure 3, step i). The acyl ligand is coordinated with the acyl-C to Re(2) and with the oxygen atom to the cation Li. The ligand is part of a distorted octahedral Re(2) and tetrahedral Li coordination sphere of nonmetal ligands. This means that the negative charge transferred by the nucleophilic attack is mainly localized on the acyl-O atom. In contrast, the negative charge of the anion [$Re_2$($\mu$-$PCy_2$)$(CO)_8$]$^-$ is situated at the central Re atoms. The anion reveals the $^{31}$P NMR signal of the $\mu$-P atom at 101.3 (s) ppm.[13] The loss of the acyl-O−Li bond in **[2$^-$]** could therefore make possible a downfield shift of the corresponding resonance ($\delta$ 63.4 (s) ppm). For this purpose and to achieve an improvement of the yield, the cation exchange of Li against $PPh_4$ was undertaken, which delivered $PPh_4$[$Re_2$($\mu$-H)($\mu$-$PCy_2$)(C(Ph)O)-

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(16) SHELXTL V5. Siemens Industrial Automation, Inc. Analytical Instrumentation, Madison, WI, 1995.

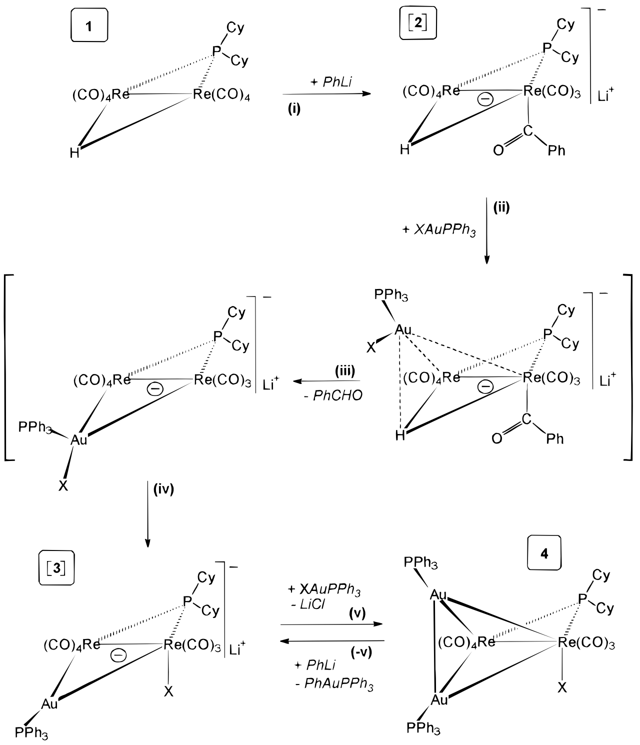

**Figure 3.** Reaction of **1** with PhLi and XAuPPh$_3$ (X = Cl, Br, I).

(CO)$_7$] (**PPh$_4$[2]**) as an air stable solid in 86% yield. Indeed, the observed $^{31}$P resonance of the $\mu$-P atom is shifted downfield to 72.3 ppm as expected. On the other hand the structural parameters of **[2$^-$]** in **PPh$_4$[2]** which were ascertained by X-ray structure analysis, show no remarkable change.[13]

To find out whether the selectivity of the LiPh attack has been a matter of serendipity since such an attack was not distinguishable by the spectroscopic data hitherto mentioned, the chiral shift reagent Eu(hfac)$_3$ was added to **PPh$_4$[2]** dissolved in CDCl$_3$. $^1$H and $^{31}$P NMR spectra showed the diastereomeric resolution of the respective peaks in an integral ratio of 1:1 (e.g. $\Delta\ \delta$ ($\mu$-P) 0.43).

**Reaction of Li[Re$_2$($\mu$-H)($\mu$-PCy$_2$)(C(Ph)O)(CO)$_7$] Li[2] with XAuPPh$_3$ (X = Cl, Br, I).** The reactivity of **Li[2]** and **PPh$_4$[2]**, respectively, toward the electrophilic complexes XAuPPh$_3$ (X = Cl, Br, I) was studied at first in the presence of 2 equiv of ClAuPPh$_3$. As the $\mu$-H deprotonated complexes [M$_2$($\mu$-PR$_2$)(CO)$_8$]$^-$ (M = Mn, Re) are known to form the triangular compounds M$_2$(AuPPh$_3$)($\mu$-PR$_2$)(CO)$_8$ when treated with ClAuPPh$_3$[4,5] and as the reaction of **1** with 2 equiv of LiPh and ClAuPPh$_3$ is known to afford the tetrahedral complex Re$_2$(AuPPh$_3$)$_2$($\mu$-PCy$_2$)($\mu$-C(Ph)O)(CO)$_6$,[4] the monoanion **[2$^-$]** should possibly be scavenged by ClAuPPh$_3$ generating an neutral chiral compound.

In a THF solution **Li[2]** was reacted with 2 equiv of ClAuPPh$_3$. A $^{31}$P NMR spectrum of the solution, recorded 15 min after addition of ClAuPPh$_3$, showed the quantitative formation of the neutral cluster complex Re$_2$(AuPPh$_3$)$_2$($\mu$-PCy$_2$)(CO)$_7$Cl **(4a)** ($^{31}$P NMR: $\delta$ 60.4 (d; $^3J_{PP}$ = 18 Hz; 1P, PPh$_3$); 64.4 (d; $^3J_{PP}$ = 18 Hz; 1P, PPh$_3$); 132.9 (s; 1P, $\mu$-P)). **4a** was identified after TLC purification (yield 92%) by means of $^1$H, $^{31}$P NMR and IR spectroscopic data. Crystallization of **4a** from CH$_2$Cl$_2$ solution in the presence of *n*-pentane led to deep yellow crystals, one of which was examined by a single crystal X-ray analysis. The molecular structure is given in Figure 2.

In compliance with the $C_1$ symmetry of **4a** in the solid state, the two Au atoms can be distinguished in solution. Thus, the $^{31}$P NMR spectra in CH$_2$Cl$_2$ or THF solution show two doublets ($^3J_{PP}$ = 18 Hz) each for the Au-bonded P atoms. The resonance at the higher field (60.4 ppm in CH$_2$Cl$_2$) is assigned to the AuPPh$_3$ group in the pseudo-trans position to the Cl ligand due to its stronger electron-donating nature compared with the CO ligand. The IR spectra show a very characteristic $\nu$(CO) vibrational pattern in accordance with the seven inequivalent CO ligands. The formation of **4a** from **[2$^-$]** and ClAuPPh$_3$ was afterward the subject of further investigations. These were undertaken because no simple mechanistic pathway was obvious and because the observed transfer of the Au-bonded Cl ligand onto the Re atom seemed rather unusual for this type of reaction.

Thus, in a first step, a THF solution of **[2$^-$]** was treated dropwise with a THF solution containing an equimolar amount of XAuPPh$_3$. After this solution was stirred at room temperature for 15 min, IR and $^{31}$P NMR spectra recorded showed the quantitative formation of a new complex anion, which was identified as [Re$_2$($\mu$-AuPPh$_3$)($\mu$-PCy$_2$)(CO)$_7$Cl]$^-$ (**[3a$^-$]**) (Figure 3). The position of the AuPPh$_3$ group trans to the bridging $\mu$-PCy$_2$ group can be derived from the chemical shifts and couplings of the $^{31}$P resonances. For this, the triangular cluster Re$_2$($\mu$-AuPPh$_3$)($\mu$-PCy$_2$)(CO)$_8$, whose structure was determined by a single X-ray analysis, can be quoted as an ideal reference.[13] $^{31}$P NMR: $\delta$ 82.2 (d; $^3J_{PP}$ = 12 Hz; 1P, PPh$_3$), 142.8 (d; $^3J_{PP}$ = 12 Hz; 1P, $\mu$-P). In addition to its spectroscopic deduction, the molecular structure of **[3a$^-$]** was also confirmed by deauration of **4a** with LiPh. Treating **4a** with one equivalent of PhLi in THF solution at low temperature, the $^{31}$P NMR spectrum of the reaction solution revealed the $^{31}$P resonances for **[3a$^-$]** besides a singlet at 44 ppm. The latter was assigned to the transmetalation product PhAuPPh$_3$. This was proved in a separate experiment by treating ClAuPPh$_3$ with PhLi (Experimental Section and Figure 3, step v). The isolation of **[3a$^-$]** as [N(PPh$_3$)$_2$][Re$_2$($\mu$-AuPPh$_3$)($\mu$-PCy$_2$)(CO)$_7$Cl] (**N(PPh$_3$)$_2$[3a]**) in a 70% yield was achieved by cation exchange from Li to [N(PPh$_3$)$_2$].

The partial steps in the formation of **[3a$^-$]** are illustrated in Figure 3 (steps ii−iv). Accordingly, the attachment of the ClAuPPh$_3$ complex to the anionic species **[3a$^-$]** effects an insertion of the $\mu$-H atom into the Re−C bond of the acyl ligand with the release of benzaldehyde. This seems to be part of a multicenter reaction process in which the Au-bonded chloro ligand refills the coordination vacancy evolved. The elimination of benzaldehyde was detected IR spectroscopically by its CO vibrational band at 1705 cm$^{-1}$. In addition, the stoichiometric generation of benzaldehyde was proved by evaporating the reaction solution (0.2 Torr, 50 °C), condensing the distillate in a cooled (−100 °C) trap and investigating the condensate by means of gas chromatography.

In a final step **Li[3a]** and **N(PPh$_3$)$_2$[3a]**, respectively, were caused to react with a second equivalent of ClAuPPh$_3$ to document their origin as precusor complexes. In both cases, **4a** was formed quantitatively, as revealed by $^{31}$P NMR measurements recorded immediately after adding ClAuPPh$_3$ (Figure 3, step v).

The reaction of **[2$^-$]** with 1 and 2 equiv of ClAuPPh$_3$ was now transferred to the homologous Au complexes BrAuPPh$_3$ and IAuPPh$_3$. Such softer halogen homologues should provide information about the specificity of the transmetalation X−Au + Re → Au + Re-X (X = Cl, Br, I) and about the stability of the resulting products. Furthermore, functionalized chiral cluster complexes of this and other types are rare. They could be of interest to anchor chiral reagents for diastereomeric separation of enantiomers and to determine the factors influencing selective metal−metal exchange. For example, the metal site selectivity with a pseudo-trans positioned AgPPh$_3$ fragment through electronically inequivalent Re atoms in the following reaction (X = Cl) is 100%:[13]

$$\mathrm{Re_2(\mu\text{-}PCy_2)X(CO)_7(AuPPh_3)_2} + \mathrm{Re_2(\mu\text{-}PCy_2)X(CO)_7(AgPPh_3)_2} \rightarrow \mathrm{Re_2(\mu\text{-}PCy_2)X(CO)_7(AuPPh_3)(AgPPh_3)}$$

The derivatives were prepared from **Li[2]** and 1 equiv of $XAuPPh_3$ (X = Br, I) as described for X = Cl. For each reaction the $^{31}P$ NMR spectra of the solutions indicated the quantitative formation of the halogenated cluster anions $[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7Br]^-$ **[3b$^-$]** and $[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7I]^-$ **[3c$^-$]**, respectively. IR spectra showed the characteristic 7 band pattern in the $\nu$ (CO) region and the formation of benzaldehyde (1705 cm$^{-1}$).

As in the case of **[3a$^-$]** the anions **[3b$^-$]** and **[3c$^-$]** could also be isolated by treating **Li[3b]**/**Li[3c]** with $[N(PPh_3)_2]Cl$ as $[N(PPh_3)_2][Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7Br]$ (**N(PPh$_3$)$_2$[3b]**) and $[N(PPh_3)_2][Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7I]$ (**N(PPh$_3$)$_2$[3c]**). Finally, the reaction of **[3b$^-$]** and **[3c$^-$]** with 1 equiv more of $BrAuPPh_3$ and $IAuPPh_3$, respectively, led to the formation of the tetranuclear cluster compounds $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7Br$ **(4b)** and $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7I$ **(4c)**, as for **[3a$^-$]**. **4b** and **4c** are air stable solids and crystallize from THF or $CH_2Cl_2$ solution shaped as very fine yellow needles. The new compounds were identified by means of IR and $^1H$ and $^{31}P$ NMR spectroscopy. The increasing electron withdrawal of the halogen ligands from I to Cl is shown by the downfield shift of the $^{31}P$ NMR signals of the respective $\mu$-P atoms (**4a**, 132.9 ppm; **4b**, 125.0 ppm; **4c**, 114.6 ppm). Furthermore, if the reactivity and stability of **[3a$^-$]**, **[3b$^-$]**, and **[3c$^-$]** and **4a**, **4b**, **4c**, respectively, were compared, no differences were observed.

**Structural Descriptions.** The molecular structures of compounds **Li[2]** and **4a** are presented in Figures 1 and 2, respectively. Crystallographic data are given in Table 1, and selected bond angles and bond lengths are given in Tables 2 and 3.

**Structure of Li[2].** The ligand arrangement at each rhenium atom is octahedrally distorted and comprises the common bridging P and H atoms of the metal centers, four carbonyl ligands at Re(1), and three carbonyl ligands and an acyl group at Re(2). The CO and the acyl ligands are arranged in eclipsed positions at both the rhenium atoms. The arrangement of the equatorial CO groups 2 and 6 with Re−Re−C angles of 115.1(4)° and 114.8(2)°, respectively, is typical for this type of structure containing a $\mu$-H bridging atom.[17−19] The Re−Re bond length from the central $Re_2P$ ring of 3.166(1) Å also compares well with those distances from related $\mu$-H-bridged dirhenium complexes.[17−19] The Re−P bond lengths are equal, the mean value of 2.455(3) Å corresponds to that of the octacarbonyl complex **1** (2.457(3) Å[17]). On the whole, there are no unexpected features concerning the geometry of the anion **[2$^-$]**. The packing of the unit cell consists of this anion, the lithium cation, one solvent water molecule, and two solvent THF molecules per asymmetric unit. Thereby, the cation reaches tetrahedral coordination by the four oxygen atoms, one from the acyl ligand and one each from the three solvent molecules. The coordination distances Li−O are 1.90(2) Å (O(8)), 1.99(3) Å (Wa), 1.98(2) Å (O(101)), and 1.91(2) Å (O(201)), respectively. The THF molecules are both disordered over two sites with occupation factors of 0.71/0.29 and 0.59/0.41 for the carbon sites and common oxygen positions.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **Li[2]**

| | | | |
|---|---|---|---|
| Re(1)−P(1) | 2.461(2) | Li(1)−O(8) | 1.90(2) |
| Re(1)−Re(2) | 3.1667(7) | Li(1)−O(201) | 1.91(2) |
| Re(2)−P(1) | 2.449(3) | Li(1)−O(101) | 1.98(2) |
| Re(2)−C(8) | 2.178(9) | Li(1)−Wa | 1.99(3) |
| C(8)−O(8) | 1.250(12) | | |
| P(1)−Re(1)−Re(2) | 49.68(6) | C(8)−O(8)−Li(1) | 131.1(10) |
| P(1)−Re(2)−Re(1) | 50.00(6) | C(2)−Re(1)−Re(2) | 115.1(4) |
| Re(2)−P(1)−Re(1) | 80.32(7) | C(6)−Re(2)−Re(1) | 114.8(3) |

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **4a**

| | | | |
|---|---|---|---|
| Au(1)−P(2) | 2.287(4) | Au(2)−Re(2) | 2.9510(11) |
| Au(1)−Au(2) | 2.6903(10) | Re(1)−Re(2) | 3.2680(10) |
| Au(1)−Re(1) | 2.9098(12) | Re(1)−P(1) | 2.442(4) |
| Au(1)−Re(2) | 2.9506(11) | Re(1)−Cl(1) | 2.549(7) |
| Au(2)−P(3) | 2.287(5) | Re(2)−P(1) | 2.464(5) |
| Au(2)−Re(1) | 2.9322(11) | | |
| P(2)−Au(1)−Au(2) | 131.92(12) | Re(1)−Au(2)−Re(2) | 67.49(3) |
| P(2)−Au(1)−Re(1) | 148.19(11) | Re(2)−Re(1)−P(1) | 48.51(9) |
| Au(2)−Au(1)−Re(1) | 63.00(3) | Re(2)−Re(1)−Cl(1) | 92.19(12) |
| P(2)−Au(1)−Re(2) | 142.04(12) | P(1)−Re(1)−Au(1) | 99.91(11) |
| Au(2)−Au(1)−Re(2) | 62.89(3) | P(1)−Re(1)−Au(2) | 98.14(11) |
| Re(1)−Au(1)−Re(2) | 67.78(3) | Au(1)−Re(1)−Au(2) | 54.84(3) |
| P(3)−Au(2)−Au(1) | 129.31(12) | Re(1)−Re(2)−P(1) | 47.95(9) |
| P(3)−Au(2)−Re(1) | 148.45(12) | P(1)−Re(2)−Au(1) | 98.32(10) |
| Au(1)−Au(2)−Re(1) | 62.16(3) | P(1)−Re(2)−Au(2) | 97.15(11) |
| P(3)−Au(2)−Re(2) | 143.24(12) | Au(1)−Re(2)−Au(2) | 54.24(2) |
| Au(1)−Au(2)−Re(2) | 62.87(3) | Re(1)−P(1)−Re(2) | 83.54(14) |

**Structure of 4a.** The compound crystallizes with one solvent $CH_2Cl_2$ molecule per asymmetric unit. The central $Re_2Au_2$ core is a slightly distorted tetrahedron. Both Au atoms have one terminal $PPh_3$ ligand, and the $\mu$-$PCy_2$ group bridges the Re−Re bond. The coordination spheres of the rhenium atoms are completed by three carbonyl and one chloro ligand at Re(1) and four carbonyl ligands at Re(2), these ligands being arranged in eclipsed positions. The cluster is saturated, fulfilling the 18 valence electron rule with the rather long Re−Re distance of 3.268(1) Å as a bonding metal−metal interaction. The substitution of one axial CO group by the chloro ligand causes the single molecule to be asymmetric. The electronic influence of these different ligand spheres at both rhenium atoms on the metallatetrahedron is clearly seen from the significant differences in the length of the Re−Au bonds which seem to be very polar ones. Re(1) with its Cl ligand shows two shorter and different bonds to Au(1) of 2.910(1) Å and to Au(2) of 2.932(1) Å, respectively, whereas the two equal Re(2)−Au bond distances are longer at 2.951(1) Å. The Au−Au bond length of 2.690(1) Å is shorter than those known from other $Re_2Au_2$ cluster compounds (2.709(2)−2.734(2) Å).[4,20]

**Conclusions and Outlook.** The described reaction with LiPh can be transferred to other lithium organyls like LiMe and Li(*n*-Bu), but a reaction temperature of about −110 °C is necessary. Such reaction conditions minimize attack at the corresponding axial carbonyl ligand of the other Re atom.

The paper shows the preparation of a chiral metallatetrahedron without any attempts to separate the enantiomers. Such separations were attempted with the usual methods, but the results were unproductive. Therefore, our efforts in this direction are directed toward diastereomeric cluster complex anions which selectively can be converted to diastereomeric metallatetrahedra. The latter could be separated by fractional crystallization.

**Supporting Information Available:** An X-ray crystallographic file in CIF format is available on the Internet only. Access information is given on any current masthead page.

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(17) Flörke, U.; Haupt, H.-J. *Z. Kristallogr.* **1992**, *201*, 295.

(18) Flörke, U.; Haupt, H.-J. *Z. Kristallogr.* **1994**, *209*, 701.

(19) Flörke, U.; Haupt, H.-J. *Z. Kristallogr.* **1994**, *209*, 702.

(20) Haupt, H.-J.; Heinekamp, C.; Flörke, U. *Z. Anorg. Allg. Chem.* **1990**, *585*, 168.