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[20] NMR experiments were performed at 22 °C in [D$_6$]DMSO at 500 MHz (Bruker DRX500 spectrometer). 2D-^{1}H DQF-COSY, TOCSY (70 ms mixing) and ROESY (200 ms mixing) spectra were acquired for resonance assignment and conformational analysis. Forty five distance constraints and three Φ dihedral angle constraints were extracted from ROESY and 1D-^{1}H spectra, respectively. A total of 100 independent structures were generated by a distance geometry algorithm, refined by two steps with a simulated annealing molecular dynamics (MD-SA; coarse + fine) protocol and sorted according to final energies. No significant violations of experimental constraints occurred for any of the calculated structures.

[21] The IC$_{50}$ values for yeast and human 20S proteasome were determined at 37 °C in the absence of SDS using the fluorogenic substrates Suc-Leu-Leu-Val-Tyr-AMC, Bz-Thr-Val-Arg-AMC and Z-Leu-Leu-Glu-βNa to assay the CT, TL, and PGPH activities following essentially protocols reported previously (G. Loidl, H.-J. Musiol, M. Groll, R. Huber, L. Moroder, *J. Pept. Sci.* **2000**, *6*, 36–46).

P_2-Ligand Complexes as Building Blocks for the Formation of One-Dimensional Polymers[**]

Junfeng Bai, Eva Leiner, and Manfred Scheer[*]

Dedicated to Professor Eckhard Herrmann
on the occasion of his 65th birthday

Self-organisation of discrete units to form supramolecular aggregates and networks of inorganic coordination compounds is a prominent field in contemporary chemistry.[1] Within this field coordination polymers are of interest with regard to their physical, electronic, catalytic, and structural properties.[2] Usual approaches in this area make use of N-donor containing ligands and heterocycles to connect different metal centers together. However, our goal in this field is to use P_n ligand complexes as connecting moieties between metal cations to form well-oriented assemblies as well as one-dimensional (1D) and two-dimensional (2D) polymers.

The coordination chemistry of P_n ligand complexes[3] towards cationic metal centers (excluding cationic organometallic complex moieties[4]) has to date been limited to the use of *cyclo*-P_3 ligand complexes, such as $[(\text{triphos})M(\eta^3\text{-}P_3)]$ (M = Co, Rh, or Ir; triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane), which react with Cu^I, Ag^I, or Au^I to form metal-bridged dimers.[5] In the reaction of the Co compound with CuBr, a multidecker complex of Co containing a $(CuBr)_6$ middle deck was obtained.[6] To generate definite polymers, P_2-ligand complexes seem to be the starting material of choice. From our experience with the chromium complex $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$[7] ($Cp = C_5H_5$) we know that this starting material readily undergoes fragmentation reactions;[8] thus, we decided to use the more stable Mo analogue **1**.[9] Herein we report the synthesis of a molecular cationic complex of Ag^I containing different and novel coordination modes of the P_2-ligand complex as well as the formation of the first 1D chain polymers of Ag^I and Cu^I containing P_2-ligand complexes.

$[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ **1**

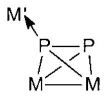
$[Ag_2\langle\{Cp_2Mo_2(CO)_4(\mu,\eta^2{:}\eta^2\text{-}P_2)\}_2\rangle$
$\langle\{Cp_2Mo_2(CO)_4(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)\}_2\rangle][(CF_3SO_3)_2]$ **2**

$[\{Re(CO)_3Br\}_2\langle\{Cp_2Mo_2(CO)_4(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)\}_2\rangle]$ **3**

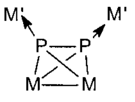
$[Ag_2\{Cp_2Mo_2(CO)_4(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)\}_3(\mu,\eta^1{:}\eta^1\text{-}NO_3)]_\infty[NO_3]_n$ **4**

$[Cu(\mu\text{-}Br)\{Cp_2Mo_2(CO)_4(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)\}]_\infty$ **5**

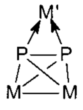
The reaction of $Ag(CF_3SO_3)$ with **1** in CH_3CN leads to the quantitative formation of **2**, in which the tetrahedral Mo_2P_2 ligand coordinates to two Ag(I) centers in a bridging as well as in a novel chelating coordination mode. Whereas the coordination of M_2P_2 tetrahedral complexes to one (type **A**) and two (type **B**) organometallic moieties is known, such as, in the type **B** situation where coordination to $[Re(CO)_3Br]$ fragments forms a central six-membered ring moiety in complex **3**,[10] the side-on coordination mode of an M_2P_2 complex at one metal center (type **C**), as found in complex **2**, is unique for a P_2-ligand complex.[3]



A



B



C

If the counterions at the Ag^I centers are noncoordinating, complexes similar to **2** are obtained.[11] However, we found a different coordination behavior if the counterion is incorporated into the coordination sphere of the Ag^I atom. Thus, the reaction of **1** with $AgNO_3$ leads to the quantitative formation of a novel polymeric Ag^I compound **4**, where one of the NO_3 counterions is now incorporated into the coordination sphere of the Ag^I atoms to form a waved 1D polymeric chain.

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Furthermore, the reaction of **1** with CuBr yields the novel linear 1D polymer **5**.

Complexes **2**, **4**, and **5** are red crystalline solids, which are stable under nitrogen and are sensitive to light in solution. They are insoluble in common solvents without decomposition; the exception being **2** which shows a slight solubility in CH$_3$CN. In the infrared (IR) spectra of all the obtained compounds, the CO stretching frequencies found are typical for terminal CO ligands. All the products have been examined by X-ray crystallography.[12]

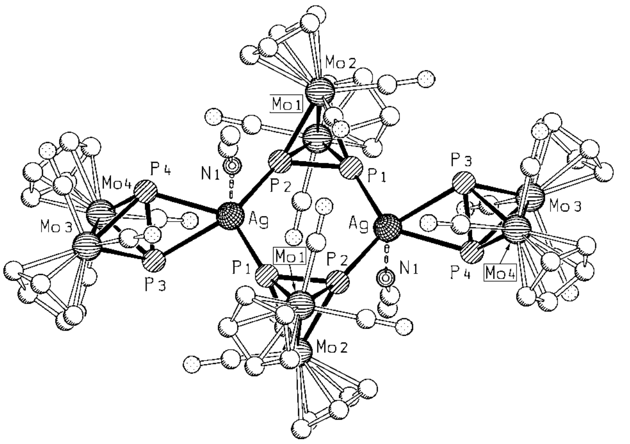

Figure 1. Molecular structure of the dianion from **2** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag-P2 2.470(1), Ag-P1 2.489(1), Ag-P4 2.610(1), Ag-P3 2.727(2), P1-P2 2.098(2), P3-P4 2.137(2); P2-Ag-P4 108.32(8), P2-Ag-P1 120.28(8), P1-Ag-P4 131.04(8), P2-Ag-P3 130.25(8), P1-Ag-P3 98.96(8), P4-Ag-P3 47.45(7).

The molecular structure of **2** (Figure 1) consists of two Ag^{I} ions bridged by two Mo$_2$P$_2$ ligand complexes, which results in a central planar six-membered ring unit (the center of which lies on the crystallographic inversion center); side-on coordinated Mo$_2$P$_2$ complexes complete the coordination sphere at the Ag^{I} ions. The [CF$_3$SO$_3$]$^-$ counterions are completely separated from the cations. The dication possesses two additional CH$_3$CN molecules, which weakly interact with the Ag atoms (Ag$\cdots$N = 2.598 Å), and this leads to a significantly distorted tetrahedral coordination environment at the Ag^{I} atoms. These CH$_3$CN molecules as well as the one in the crystal lattice of **2** are easily lost if the compound is dried under vacuum. The bond lengths and angles of the bridging bidentate Mo$_2$P$_2$ fragments are similar to those found in other complexes, such as **3**,[10] and, furthermore, they differ very little from those in the uncoordinated molecule **1**.[9] The predominant difference between **2** and compounds **1** and **3** is the slightly longer bridging P−P bond (2.098(2) Å compared to 2.079(2) Å in **1** and 2.071(9) Å in **3**). More interesting is the comparison of the P−P bond lengths within **2**, where the chelating bond (2.137(2) Å) is much longer than the bridging one. The same trend is observed for the Ag−P distances, where the chelating Ag−P bonds (2.610(1) and 2.727(2) Å) are significantly longer than those of the central six-membered ring moiety (2.487(2) Å and 2.470(2) Å). However, in the ion [Ag(P$_4$)$_2$]$^+$,[13] where two P$_4$ units coordinate side-on at a Ag^{I} center, the Ag−P (2.536(2)–2.548(1) Å) as well as the P−P (2.328(2) and 2.330(2) Å) bond lengths are significantly longer than in the side-on bound (chelating) Mo$_2$P$_2$ moiety of **2**.

A view of the waved 1D chain structure of complex **4** is depicted in Figure 2. In **4** two different Ag^{I} atoms are each connected by bridging Mo$_2$P$_2$ units, to give two crystallographically distinct planar six-membered ring moieties (the center of each lies on a crystallographic inversion center), and are linked together by a third Mo$_2$P$_2$ unit and a bridging NO$_3^-$ ion, to form an additional seven-membered Ag$_2$NO$_2$P$_2$ ring system. The novel waved 1D chain of the cation is formed by alternating planar six-membered rings and novel seven-membered rings, in which each Ag^{I} center is in a distorted tetrahedral coordination environment. Whereas the bond lengths and angles of the six-membered ring, formed by the atoms Ag2, P5, and P6, are similar to those found for complex **2**, the second planar six-membered ring of **4**, formed by the atoms Ag1, P1, and P2, exhibits slightly lengthened P−P (2.097(2) Å, compared to 2.089(1) Å in **2**) and Ag−P (2.520(1) and 2.544(1) Å) bonds. This lengthening is caused by the influence of the different coordination modes of the bridging nitrate anion. Thus, the Ag2−O14 bond (2.526(3) Å), perpendicular to the plane of the nitrate anion, is longer than the Ag1−O13 bond (2.500(3) Å) which lies in the plane of the nitrate anion. Each of these bond lengths is in the range of reported Ag−O bonds (2.367–2.689 Å).[14] Thus, shorter Ag−O bonds give longer Ag−P and P−P bonds in the six-

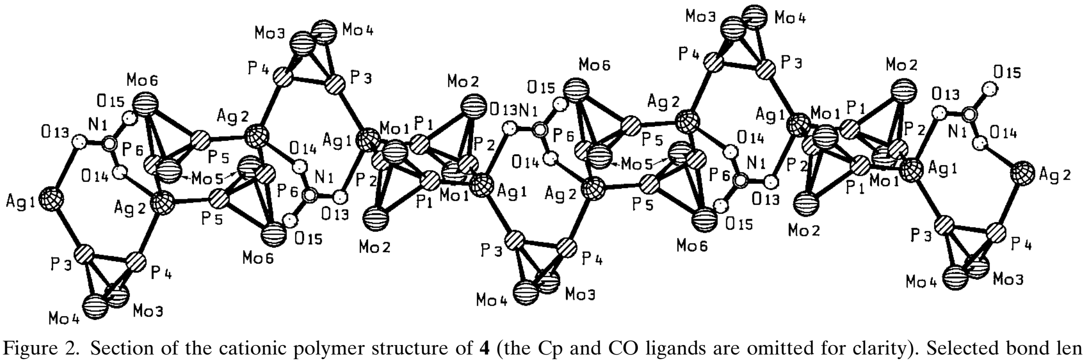

Figure 2. Section of the cationic polymer structure of **4** (the Cp and CO ligands are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.097(2), P3-P4 2.099(2), P5-P6 2.089(1), Ag1-P3 2.495(1), Ag1-O13 2.500(3), Ag1-P1 2.520(1), Ag1-P2 2.544(1), Ag2-P6 2.478(1), Ag2-P4 2.492(1), Ag2-P5 2.498(1), Ag2-O14 2.526(3); P3-Ag1-O13 119.70(8), P3-Ag1-P1 111.35(3), O13-Ag1-P1 96.76(7), P3-Ag1-P2 119.31(4), O13-Ag1-P2 92.08(8), P1-Ag1-P2 114.43(4), P6-Ag2-P4 122.06(3), P6-Ag2-P5 119.49(4), P4-Ag2-P5 111.56(4), P6-Ag2-O14 97.61(6), P4-Ag2-O14 96.89(7), P5-Ag2-O14 101.99(7).

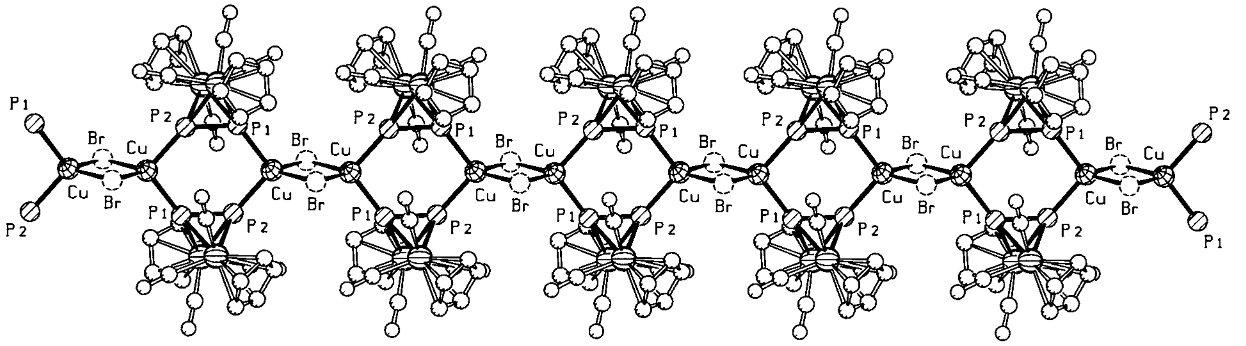

Figure 3. Section of the 1D polymer chain structure of **5** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.068(3), Cu-P 2.288(2), Cu-Br 2.465(1); P-Cu-P 102.02(10), P-P-Cu 128.99(5), Cu-Br-Cu 71.61(5), Br-Cu-Br 102.39(5).

membered rings and vice versa. Furthermore, the distance between the atoms O14 and Ag1 is 2.833(3) Å which indicates that there is a weak interaction between them.

In Figure 3 the linear 1D chain structure of **5** is depicted as consisting of planar six-membered Cu_2P_4 and four-membered Cu_2Br_2 rings, alternately arranged in an orthogonal manner. The coordination geometry at the Cu^I center is tetrahedral. The Cu^I atoms in **5** are symmetrically bound to the Br and P atoms. The P–P bond lengths in the P_2 units of **5** (2.079(1) Å) are similar to those in complex **3** (2.071(9) Å)[10] and in the uncoordinated complex **1** (2.079(2) Å)[9] but shorter than in the Ag^I complexes **2** and **4**. Furthermore, the bond lengths and angles of the bridging bidentate Mo_2P_2 fragments are similar to those found in the uncoordinated molecule **1**. The Cu–P bonds of **5** (2.288(1) and 2.297(1) Å) are slightly shorter than those in $[\{(triphos)CoP_3\}_2Cu]PF_6 \cdot 2THF$ (2.360(2), 2.320(2), 2.303(2), and 2.329(2) Å). The Cu–Br bond of **5** (2.466(1) Å) is within the range displayed by the bromide-bridged complex $[Cu_2(PPh_3)_3Br_2]$ (2.370(2)–2.610(2) Å).[15] The formation of **5** shows on the one hand the different coordination behavior of the Mo_2P_2 complex **1** with CuBr compared to the *cyclo*-P_3 complexes $[(triphos)M(\eta^3\text{-}P_3)]$ (M = Co, Rh, or Ir) with CuBr.[6] On the other hand there are similarities to the recently discovered use of copper(I) halides as matrices for the synthesis of novel ion-conducting materials.[16]

In the ^{31}P NMR spectrum of complex **2** (CD_3CN) at room temperature, only one singlet is observed ($\delta = -69.0$). The chemical shift appears considerably upfield with respect to uncoordinated complex **1** ($\delta = -41.5$). Recording the ^{31}P NMR spectrum at the lowest possible temperature (−30 °C)[17] led to an upfield shift ($\Delta\delta = 14.7$ ppm) and to a significant broadening of the signal. Thus we assume for **2** in solution a fluxional process, where the coordination modes of the different Mo_2P_2 ligands are in fast exchange. Additional solid-state ^{31}P NMR studies to prove the different nature of the P atoms of **2** and also of **4** are in progress.

In conclusion, the results have shown that the Mo_2P_2 tetrahedral complex **1** seems to be an efficient starting material as a linker unit in supramolecular aggregates. Furthermore, it reveals that the influence of the counterion is crucial for the formation of a molecular or a polymeric structure. Thus, the use of noncoordinating counterions leads to molecular units, whereas the presence of coordinating counterions results in 1D polymeric structural frameworks.

Experimental Section

2: A solution of $Ag(CF_3SO_3)$ (25.7 mg, 0.1 mmol) in CH_3CN (25 mL) was added to a solution of **1** (99 mg, 0.2 mmol) in CH_3CN (15 mL) at 0 °C. This mixture was stored at −30 °C for two days and red crystals of **2** (93 mg, 0.15 mmol, 75 %) were formed. The product was collected by filtration and washed with CH_3CN (15 mL) and then dried under vacuum. IR (KBr): $\tilde{\nu} =$ 1992 (vs), 1938 (vs), 1919 (vs) cm^{-1} (CO); $^{31}P\{^1H\}$ NMR (101 MHz, CD_3CN, 25 °C): $\delta = -69.0$ (s, $\omega_{1/2} = 100$ Hz); $^{31}P\{^1H\}$ NMR (CD_3CN, −30 °C): $\delta = -83.7$ (s, $\omega_{1/2} = 200$ Hz); Elemental analysis (%) calcd for $C_{29}H_{20}O_{11}P_4SAgF_3Mo_4$ (1249.05): C 27.89, H 1.61; found: C 28.33, H 1.82.

4: A solution of $AgNO_3$ (34 mg, 0.2 mmol) in CH_3CN (25 mL) was added to a solution of **1** (99 mg, 0.2 mmol) in CH_3CN (15 mL) at 0 °C. This mixture was stored at −30 °C for two days and red crystals of **4** (110 mg, 0.18 mmol, 90 %) were formed. The product was collected by filtration and washed with CH_3CN (15 mL) and then dried under vacuum. IR (KBr): $\tilde{\nu} = 2349$ (w) (CN), 2018 (w), 1970 (s), 1919 (vs), 1863 (m), 1837 (w) (CO), 1384 (vs) cm^{-1} (NO_3); Elemental analysis (%) calcd for $\mathbf{4} \cdot 3CH_3CN$: $C_{48}H_{39}N_5O_{18}P_6Ag_2Mo_6$ (1951.08): C 29.55, N 3.59, H 2.01; found: C 29.36, N 3.09, H 2.30.

5: A solution of CuBr (57 mg, 0.4 mmol) in CH_3CN (10 mL) was added at room temperature to a solution of **1** (100 mg, 0.2 mmol) in CH_3CN (10 mL), and a red precipitate of **5** appeared instantly. Further stirring for 1 h at room temperature led to the complete formation of **5** (112 mg, 0.174 mmol, 87 %), which was collected by filtration, washed with CH_3CN (3 × 25 mL), and dried under vacuum. Single crystals of **5** were obtained by very slow diffusion of CH_3CN solutions of the starting materials. IR (KBr): $\tilde{\nu} = 2008$ (vs), 1962 (s), 1928 (vs), 1861 (s), 1834 (s) cm^{-1} (CO); Elemental analysis (%) calcd for $C_{14}H_{10}BrCuMo_2O_4P_2$ (639.51): C 26.29, H 1.58; found: C 26.69, H 1.42.

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[12] Crystal-structure analyses of **2** and **4** were performed on a STOE IPDS diffractometer and the analysis of **5** on a Bruker AXS/CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with the program SHELXS-93,[18a] and full-matrix least-squares refinement on F^2 in SHELXL-97[18b] was performed with anisotropic displacements for non-hydrogen atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **2**$\cdot 3\,CH_3CN$ (two molecules of CH_3CN are coordinated to the Ag^I centers and one is co-crystallized in the crystal lattice): $C_{35}H_{29}AgF_3Mo_4N_3O_{11}P_4S$, $M_r = 1372.18$, crystal dimensions $0.20 \times 0.12 \times 0.04$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.160(2)$, $b = 13.597(3)$, $c = 15.584(3)$ Å, $\alpha = 114.63(3)$, $\beta = 98.53(3)$, $\gamma = 94.16(3)^\circ$, $T = 200(1)$ K, $Z = 2$, $V = 2290.3(8)$ Å^3, $\rho_{calcd} = 1.990$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.740$ mm^{-1}, 8286 independent reflexes ($R_{int} = 0.0299$, $2\theta_{max} = 52^\circ$), 6863 observed with $F_o = 4\sigma\ (F_o)$, 575 parameters, $R_1 = 0.0310$, $wR_2 = 0.0807$. **4**$\cdot 3\,CH_3CN$ (all molecules CH_3CN are co-crystallized in the crystal lattice): $C_{48}H_{39}Ag_2Mo_6N_5O_{18}P_6$, $M_r = 1951.04$, crystal dimensions $0.30 \times 0.20 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$ (No. 2); $a = 13.895(3)$, $b = 15.702(3)$, $c = 15.772(3)$ Å, $\alpha = 114.19(3)$, $\beta = 94.23(3)$, $\gamma = 91.44(3)^\circ$, $T = 200(1)$ K, $Z = 2$, $V = 3124.4(11)$ Å^3, $\rho_{calcd} = 2.074$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 2.000$ mm^{-1}, 11 347 independent reflexes ($R_{int} = 0.0240$, $2\theta_{max} = 52^\circ$), 10 117 observed with $F_o = 4\sigma\ (F_o)$; 769 parameters, $R_1 = 0.0268$, $wR_2 = 0.0711$. **5**: $C_{14}H_{10}BrCuMo_2O_4P_2$, $M_r = 639.49$, crystal dimensions $0.10 \times 0.04 \times 0.02$ mm^3, monoclinic, space group $P2_{1/n}$ (No. 14), $a = 14.8302(16)$, $b = 8.0476(9)$, $c = 16.2654(18)$ Å, $\beta = 111.414(2)^\circ$, $T = 200(1)$ K, $Z = 4$, $V = 1807.2(3)$ Å^3, $\rho_{calcd} = 2.350$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 4.935$ mm^{-1}, 4073 independent reflexes ($R_{int} = 0.0727$, $2\theta_{max} = 56^\circ$), 2844 observed with $F_o = 4\sigma\ (F_o)$, 217 parameters, $R_1 = 0.0325$, $wR_2 = 0.0669$. CCDC 170717–170719 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Tetra- and Pentacyclopropylcyclopentadiene—Two New Donor-Substituted Ligands for Metal Complexes**

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Dedicated to Professor Oskar Glemser
on the occasion of his 90th birthday

Ligand tuning undoubtedly is one of the most important tools to modify the properties of metal complexes, for example to enhance the catalytic activity and stereoselectivity in metal-catalyzed reactions. Both the electronic and steric factors play an important role in this context. Among the most frequently used ligands are cyclopentadiene and its substituted analogues.[1] Although a great variety of substituted cyclopentadienes have been prepared, very little is known about cyclopropyl-substituted derivatives. Yet the cyclopropyl group has unique electronic properties[2, 3] in that it is a particularly good donor for electron-deficient centers, and sterically it is closer to an ethyl than to an isopropyl group.[4] We here report on the first synthesis of tetra- and pentacyclopropylcyclopentadiene[5] and some of their metal complexes.

Applying the protocol of Sato et al. for the hydromagnesation of alkynes,[6] the easily accessible dicyclopropylacetylene (**1**),[7] by treatment with isobutylmagnesium bromide in the presence of titanocene dichloride (1 mol%) in diethyl ether, was transformed to 1,2-dicyclopropylethenylmagnesium bromide (**2**) which, when added to a solution of *n*-butyl formate in tetrahydrofuran, gave 1,2,4,5-tetracyclopropylcyclopentadiene (**3**) right away in 56% yield (Scheme 1). The expected 1,2,4,5-tetracyclopropylpenta-1,4-dien-3-ol (**10**, R = H) was isolated in poor yield along with an isomer and a lot of polymeric material only when the *n*-butyl formate was added to the solution of the Grignard reagent **2**. In fact, the dienol **10** could not be converted to the cyclopentadiene **3** under the conditions that have been established for the conversion of

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