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Communications

Annular Heterometallic Stars[†]

Edwin C. Constable,* Catherine E. Housecroft,* Bénédicte Krattinger,
Markus Neuburger, and Margareta Zehnder

*Institut für Anorganische Chemie, Universität Basel, Spitalstrasse 51,
CH-4056 Basel, Switzerland*

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Summary: A new class of arene-centered star molecules in which two different types of organometallic domains are sequentially introduced to specifically generate hetero-polynuclear compounds is described.

We are interested in methodology development for the synthesis of metal-rich star and dendritic compounds which may be used as precursors to new materials.[1] Recently, we reported the formation of $[H\{C{\equiv}C\text{-}p\text{-}C_6H_4\}_n]_4C$ (n = 1, 2, 3) and subsequent reactions with $[Co_2(CO)_8]$ to give star molecules with rigid, cluster-containing arms.[2] A number of groups have reported organometallic compounds of the type $1,3,5\text{-}(XC{\equiv}C)_3C_6H_3$,[3–6] with the emphasis on M–C σ-bond formation, or both alkyne and vinylidene derivatives.[3] In this paper, we describe a new class of arene-centered star molecules in which two different types of organometallic domains are introduced stepwise to specifically generate hetero-polynuclear compounds. Synthetic transformations are summarized in Scheme 1.

The compound $1,3,5\text{-}(Ph_2PC{\equiv}C)_3C_6H_3$, **1**, was prepared adapting the method of Liu et al.[7] by treatment of $1,3,5\text{-}(HC{\equiv}C)_3C_6H_3$[8–10] with ^nBuLi and Ph_2PCl in THF.[11] This tridentate phosphine ligand reacts readily with $[Mo(CO)_5(THF)]$ or $[W(CO)_5(THF)]$ (generated in situ from $M(CO)_6$, M = Mo or W) to give the trimetallic

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[†] Dedicated to Professor John Osborn on the occasion of his 60th birthday.

* Corresponding authors: Fax: +41 61 267 1014. Tel: +41 61 267 1004. E-mail: housecroft@ubaclu.unibas.ch.

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(11) **1**: ^nBuLi (4.00 mmol) was added dropwise to $1,3,5\text{-}(HC{\equiv}C)_3C_6H_3$ (200 mg, 1.33 mol) in THF (20 mL) at 253 K. The reaction mixture was stirred for 20 min, and then Ph_2PCl (878 mg, 4.00 mmol) was added. After extraction and chromatographic workup, **1** was recrystallized from CH_2Cl_2/MeOH (908 mg, 98%; mp 109 °C). IR (CH_2Cl_2, cm^{-1}): 2184 vw, 1577 s, 1479 w. ^1H NMR (300 MHz, $CDCl_3$): δ 7.4–8.0 (m). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 88.4 (d, J_{CP} 10.2 Hz, $P\mathit{C}C$), 105.5 (d, J_{CP} 2.8 Hz, $PC\mathit{C}$), 123.7 (s, C_{arene}), 128.8 (d, J_{CP} 7.4 Hz, $C_{Ph}{}^{3,5}$), 129.3 (s, $C_{Ph}{}^4$), 132.7 (d, J_{CP} 20.7 Hz, $C_{Ph}{}^{2,6}$), 134.8 (s, $C_{arene}H$), 135.7 (d, J_{CP} 5.8 Hz, $C_{Ph}{}^{ipso}$). ^{31}P (121 MHz, $CDCl_3$): δ −33.7 (s). MS (FAB, NBA-matrix): m/z 702 $[M]^+$ (NBA = 3-nitrobenzyl alcohol).

(12) **2:** A THF (40 mL) solution of $[Mo(CO)_6]$ (94 mg, 0.20 mmol) was irradiated for 3 h under a stream of argon. **1** (50 mg, 0.071 mmol) was added and the reaction mixture stirred for 3 h. Chromatographic workup and recrystallization from CH_2Cl_2/MeCN gave light yellow **2** (72 mg, 72%; mp 137 °C). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2178 vw, 2075 s, 1985 w, 1949 vs. ^1H NMR (300 MHz, $CDCl_3$): δ 7.4–7.6 (m, 18H, Ph), 7.7–7.8 (m, 12H, Ph), 7.82 (s, 3H, arene). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 86.2 (d, J_{CP} 67.5 Hz, $P\mathit{C}C$), 107.0 (d, J_{CP} 11.8 Hz, $PC\mathit{C}$), 122.8 (s, C_{arene}), 128.9 (d, J_{CP} 10.4 Hz, $C_{Ph}{}^{3,5}$), 130.6 (s, $C_{Ph}{}^4$), 131.3 (d, J_{CP} 14.5 Hz, $C_{Ph}{}^{2,6}$), 134.6 (d, J_{CP} 45.7 Hz, $C_{Ph}{}^{ipso}$), 136.4 (s, $C_{arene}H$), 205.1 (d, J_{CP} 8.7 Hz, $\mathit{C}O$), 209.8 (d, J_{CP} 23.8 Hz, $\mathit{C}O$). ^{31}P (121 MHz, $CDCl_3$): δ +13.0 (s). MS (FAB, NBA-matrix): m/z 1411 $[M]^+$ with correct isotopomers.

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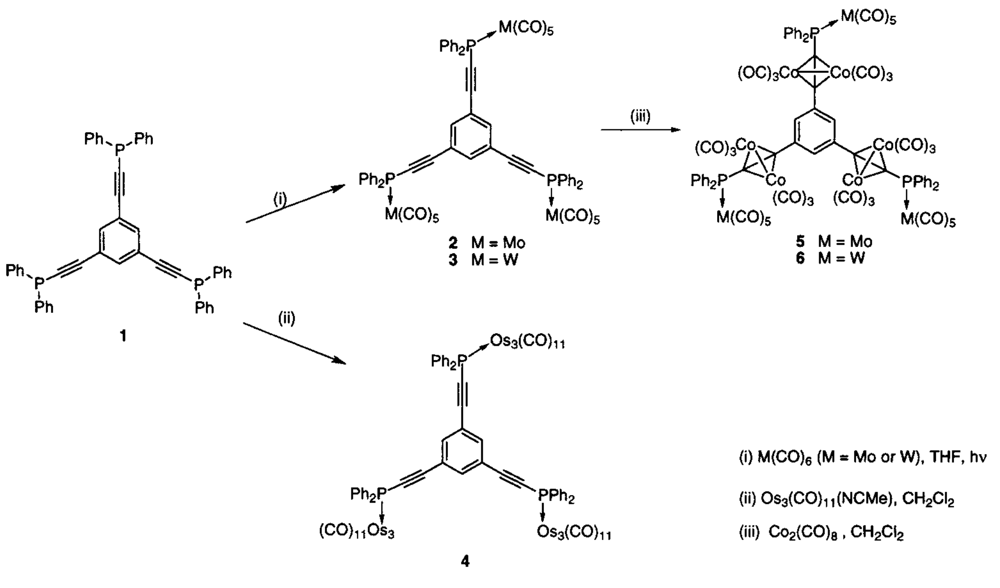
Scheme 1



derivatives **2** and **3**, respectively; conditions for the formation of **3** are similar to those of **2**,[12] and satisfactory elemental analytical, spectroscopic, and mass spectrometric data were obtained for both **2** and **3**. In the ^{31}P NMR spectra, a shift to lower field on going from **1** to **2**, or from **1** to **3**, is diagnostic of phosphorus-coordination, and the magnitude of the shift difference $\Delta\delta = (\delta_{\mathrm{complex}} - \delta_{\mathrm{ligand}})$ is close to that observed on going from PPh_3 to $[Mo(CO)_5(PPh_3)]$ or $[W(CO)_5(PPh_3)]$, respectively.[13] Furthermore, in the ^{31}P NMR spectrum of **3**, satellite peaks were observed with $J_{PW} = 244$ Hz. X-ray quality crystals of **2**[14] were grown by slow evaporation of an Et_2O/MeCN solution. The structure of **2** is shown in Figure 1, and selected bond distances and angles are given in the caption. The phosphorus atoms, central benzene ring, and alkyne units are essentially coplanar; the three octahedral molybdenum centers are oriented above the same face of the benzene core. The structural analysis confirms the lack of steric crowding around the metal centers and indicates that reactions of **1** with multinuclear metal carbonyl clusters should be viable. Indeed, compound **1** reacts with an excess of $[Os_3(CO)_{11}(NCMe)]$[15] to give the nonaosmium star compound **4**,[16] which has been characterized by spectroscopic and mass spectrometric methods; satisfactory elemental analysis was obtained.

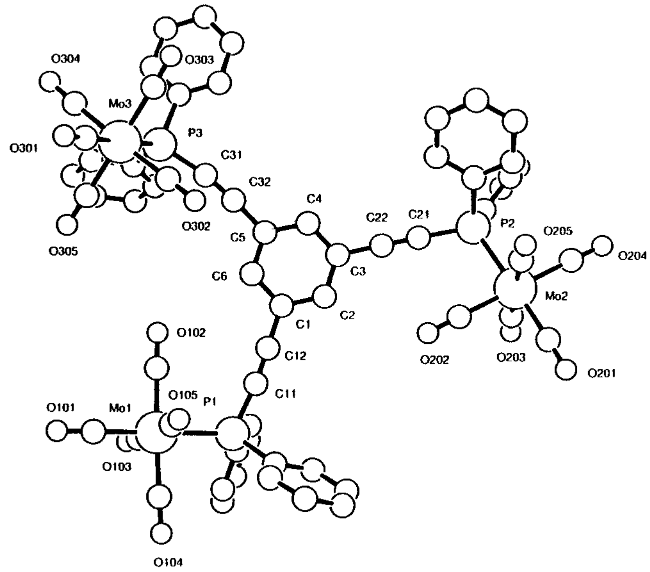


Figure 1. Molecular structure of compound **2**; H atoms are omitted. Selected bond distance (Å) and angles (deg): Mo(1)−P(1) = 2.5080(8), Mo(2)−P(2) = 2.4938(8), Mo(3)−P(3) = 2.509(1), P(1)−C(11) = 1.762(3), P(2)−C(21) = 1.764(4), P(3)−C(31) = 1.760(3), C(11)−C(12) = 1.200(5), C(21)−C(22) = 1.195(5), C(31)−C(32) = 1.194(5); Mo(1)−P(1)−C(11) = 112.7(1), Mo(2)−P(2)−C(21) = 113.1(1), Mo(3)−P(3)−C(31) =113.0(2).

It has previously been demonstrated by Bruce and coworkers[17,18] that one alkyne group adjacent to a PPh_2 unit in $[(OC)_{11}M_nPh_2PC{\equiv}CC{\equiv}CPPh_2M_n(OC)_{11}]$ (M_n = Ru_3, Os_3, Re_3H_3, or Ru_4H_4) and related mononuclear species reacts with $[Co_2(CO)_8]$ in the expected manner[19−21] to yield a $\{C_2Co_2(CO)_6\}$ cluster unit. In these

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(14) Crystal data for **2**: $C_{63}H_{33}Mo_3O_{15}P_3.0.5C_4H_{10}O$, triclinic, $P\bar{1}$ (No. 2), $a = 15.487(2)$ Å, $b = 15.712(5)$ Å, $c = 16.826(1)$ Å, $\alpha = 94.93(2)°$, $\beta = 115.609(8)°$, $\gamma = 110.51(2)°$, $U = 3318.7(13)$ Å^3, $Z = 2$, $M = 1447.74$, $D_c = 1.449$ g cm^{-3}, $\mu = 5.88$ mm^{-1}. Single-crystal X-ray diffraction data were recorded at 293 K (Cu Kα radiation) with θ min/max = 2/77.5°; 13385 measured reflections; 12911 independent reflections; $R = 0.0465$; $R_w = 0.0591$.

(15) Nicholls, J. N.; Vargas, M. D. *Inorg. Synth.* **1990**, *28*, 232.

(16) **4**: $[Os_3(CO)_{11}(NCMe)]$ (145 mg, 0.157 mmol) was added to **1** (22 mg, 0.031 mml) in CH_2Cl_2 (10 mL) and the solution stirred for 3 h. After chromatographic workup and recrystallization from hexane, **4** was obtained as a yellow powder (55 mg, 58%, mp 120 °C). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2178 vw, 2055 vs, 2035 vs, 2018 vs, 1988 w, 1980 w, 1961 sh. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3−7.6 (m, 18H, Ph), 7.6−7.8 (m, 12H, Ph), 7.83 (s, 3H, arene). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 87.0 (d, J_{CP} 94.7 Hz, PCC), 106.4 (d, J_{CP} 14.9 Hz, PCC), 122.4 (s, C_{arene}), 128.9 (d, J_{CP} 11.6 Hz, $C_{Ph}{}^{3,5}$), 130.9 (s, $C_{Ph}{}^{4}$), 131.0 (d, J_{CP} 12.7 Hz, $C_{Ph}{}^{2,6}$), 134.4 (d, J_{CP} 62.5 Hz, $C_{Ph}{}^{ipso}$), 136.4 (s, C_{arene}H). ^{31}P (121 MHz, $CDCl_3$): δ −35.0 (s). MS (FAB, NBA-matrix): m/z 3340 $[M]^+$ with correct isotopomers.

(17) Adams, C. J.; Bruce, M. I.; Horn, E.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1993**, 3313.

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compounds, the PC≡CC≡CP spacer (as opposed to PC≡CP spacer) appears to be important on steric grounds.[17] Despite the fact that the alkyne units in **2** and **3** are somewhat more hindered, each compound reacts smoothly with an excess of $[Co_2(CO)_8]$ giving compounds **5** and **6**, respectively. These compounds contain inner shells of three $\{Co_2C_2(CO)_6\}$ cluster units. The experimental procedure for **5** is analogous to that for **6**.[22] The ^{1}H and ^{13}C NMR spectra of **5** and **6** were in accord with symmetrical products, i.e. in which all three alkyne functionalities had reacted; to date, we have not obtained X-ray quality crystals of **5** or **6**. Preliminary results indicate that compound **4** also reacts with an excess of $[Co_2(CO)_8]$ to give heterometallic star species similar to **5** and **6**; the reaction, however, is very slow, and full details will be reported in a subsequent paper.

The properties of these novel star systems are currently under investigation, as is the extension of the methodology to related heterometallic compounds.

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Supporting Information Available: Details about the X-ray structure of **2**, including an ORTEP diagram and tables of crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available in CIF format from cif.om@acs.org.

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(22) **6**: $[Co_2(CO)_8]$ (183 mg, 0.54 mmol) was added to a CH_2Cl_2 (140 mL) solution of **3** (60 mg, 0.036 mmol) and the mixture stirred for 3 h. Chromatographic workup (silica, CH_2Cl_2:hexane 1:7) and recrystallization from CH_2Cl_2/hexane gave purple crystals of **6** (60 mg, 67%; mp 157 °C). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2098 w, 2071 s, 2041 w, 1989 vw, 1936 vs. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4−7.6 (m, 18H, Ph), 7.70 (s, 3H, arene), 7.7−7.8 (m, 12H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 92.3 (d, J_{CP} 7.9 Hz, P*C*C), 105.3 (d, J_{CP} 8.3 Hz, PC*C*), 120.0 (br, C_{arene}), 128.8 (d, J_{CP} 9.6 Hz, $C_{Ph}{}^{3,5}$), 130.8 (s, $C_{Ph}{}^4$), 132.5 (d, J_{CP} 12.1 Hz, $C_{Ph}{}^{2,6}$), 138.9 (d, J_{CP} 43.9 Hz, $C_{Ph}{}^{ipso}$), 140.4 (s, $C_{arene}H$), 197.1 (d, J_{CP} 6.6 Hz, *C*O), 197.8 (br, *C*O), 198.8 (d, J_{CP} 23.5 Hz, *C*O). ^{31}P (121 MHz, $CDCl_3$): δ −25.4 (pseudo-t, J_{PW} 244.5 Hz). MS (FAB, NBA-matrix): *m/z* 2533 $[M]^+$, 2248 $[M - Co_2(CO)_6]^+$ with correct isotopomers.