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An Organometallic Octopus Complex: Structure and Properties of a Resorcinarene with 16 Cobalt Centers

Dana Eisler, Wei Hong, Michael C. Jennings, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

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An "octopus-like" octapropargyl resorcinarene gives the most highly metalated resorcinarene known by addition of $Co_2(CO)_6$ units to all eight propargyl groups. Reaction of the octapropargyl resorcinarene derivatives $\{PhCH_2CH_2CHC_6H_2(OCH_2CCR)_2\}_4$ (R = H, Me) with $[Co_2(CO)_8]$ gives the corresponding octakis[alkyne(dicobalt)] derivatives $[\{PhCH_2CH_2CHC_6H_2(OCH_2CCRCo_2(CO)_6)_2\}_4]$, and the Co_{16} complex with R = H has been structurally characterized. The octapropargyl compound $\{PhCH_2CH_2CHC_6H_2(OCH_2CCH)_2\}_4$ also yields the octaalkynylgold(I) derivatives $[\{PhCH_2CH_2CHC_6H_2(OCH_2CCAuL)_2\}_4]$, with L = PPh_3, *t*-BuNC, and the insoluble, polymeric compounds $[\{PhCH_2CH_2CHC_6H_2(OCH_2CCAu)_2(\mu\text{-}LL)_2\}_4]_x$ with diphosphine ligands, with LL = $Ph_2P(CH_2)_nPPh_2$ and $n = 1, 2, 4$.

Introduction

There has been intense interest in the synthesis and applications of metalated calixarenes and resorcinarenes.[1−4] For example, resorcinarenes may be metalated by binding directly to the oxygen atoms of the upper rim,[5] after incorporation of nitrogen, phosphorus, sulfur, or other donors at the upper rim,[6,7] or by incorporation during the resorcinarene synthesis.[8] The majority of known transition-metal resorcinarene complexes contain 1−4 metal atoms.[1−8] However, the effects of multiple metal atom incorporation are of interest and several complexes with 8 metal atoms, and one with 12 ferrocenyl groups, have been prepared.[7] These highly metalated complexes have been well characterized by spectroscopic methods, but there are little structural data available, since they are difficult to crystallize.[7] This article reports the synthesis of two octaalkynyl resorcinarenes and their octakis$[Co_2(CO)_6]$ derivatives. The octapropargyl resorcinarene and its cobalt derivative have been structurally characterized, thus allowing the effects of multiple metalation on the structure and dynamics of the resorcinarene skeleton to be defined for the first time. The complexes with 16 cobalt atoms are the most highly metalated resorcinarenes known; the structure resembles an octopus, with a resorcinarene body and eight propargyl tentacles, each bound to a dicobalt unit.

Results and Discussion

Synthesis of the Resorcinarenes and Their Metal Complexes. The eight hydroxyl groups of the known resorcinarene **1**[9] (Chart 1) were converted to propargyloxy groups in **2** by reaction with propargyl bromide in the presence of K_2CO_3 as base.[10] Similarly, reaction of **1** with 1-bromo-2-butyne resulted in the formation of the octa-2-butynyl resorcinarene **3**. These alkyne derivatives are useful for assembling metal complexes at the rim of the resorcinarene bowl, and the octapropargyl resorcinarene **2** is a particularly versatile reagent for organometallic synthesis, since it may give octa-σ-alkynyl or octa-π-alkyne derivatives.

Two routes to alkynylgold complexes derived from **2** were developed. In the first method, the reaction of **2** with $[AuCl(PPh_3)]$ and base gave the air-stable but light-sensitive octaalkynylgold complex **4** (Chart 1). In the

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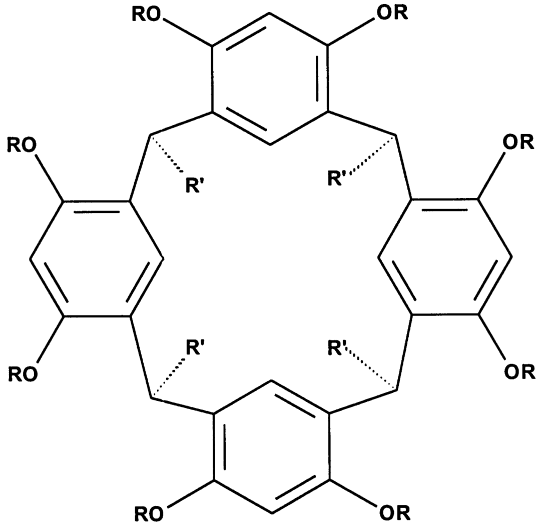
Chart 1[a]



1, R = H

2, R = $CH_2C{\equiv}CH$

3, R = $CH_2C{\equiv}CCH_3$

4, R = $CH_2C{\equiv}CAuPPh_3$

5, R = $CH_2C{\equiv}CAuCNC(CH_3)_3$

6, R = 0.5 $[(CH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$

7, R = 0.5 $[(CH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_2PPh_2)]$

8, R = 0.5 $[(CH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)]$

9, R = $CH_2C{\equiv}CH\{Co_2(CO)_6\}$

10, R = $CH_2C{\equiv}CCH_3\{Co_2(CO)_6\}$

[a] R′ = CH_2CH_2Ph.

second method, the resorcinarene **2** was reacted with base and $[AuCl(SMe_2)]$ to give an insoluble gold acetylide, probably containing both (σ-alkynyl)gold(I) and (π-alkyne)gold(I) groups,[11] and this intermediate was then treated with *tert*-butyl isocyanide to give the octagold resorcinarene complex **5** (Chart 1). The molecular structures of **4** and **5** were defined by their NMR spectra, but suitable crystals for stucture determination could not be grown. Reaction of complex **5** with diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (with $n = 1, 2, 4$) led to precipitation of the corresponding diphosphinegold(I) complexes **6**−**8**, in which the diphosphines bridge between gold(I) centers, as insoluble white solids.

The reactions of **2** and **3** with excess $[Co_2(CO)_8]$ gave the corresponding alkynedicobalt derivatives **9** and **10**. These complexes **9** and **10** each contain 16 metal atoms on the upper rim of the resorcinarene, and this appears to be a record for metalation of resorcinarenes. Complexes **9** and **10** are red solids that are only slowly decomposed by air, over days in solution or weeks in the solid state.

Characterization of the Compounds. The structures of the octapropargyl resorcinarene **2** and its cobalt carbonyl derivative **9** (Chart 1) have been determined and provide benchmarks for characterization of the other compounds by spectroscopic methods. Comparison of the structures of **2** (Figure 1) and **9** (Figure 2) shows the structural consequences of adding the eight dicobalt units. The structure determination for **9** confirms the presence of typical (alkyne)$Co_2(CO)_6$ groups, with roughly tetrahedral Co_2C_2 alkynedicobalt units, and the associated bond angles and distances are unremarkable.[13]

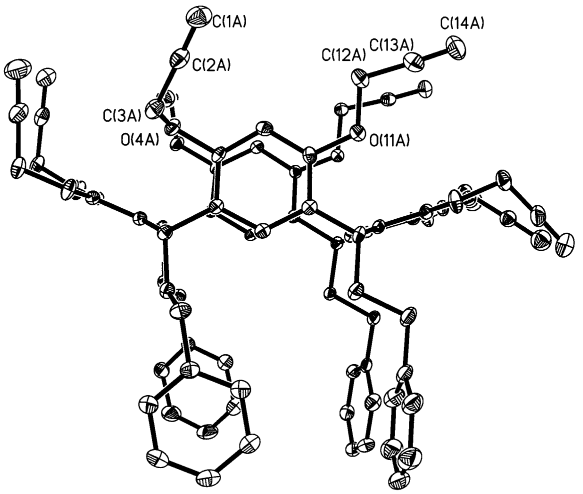
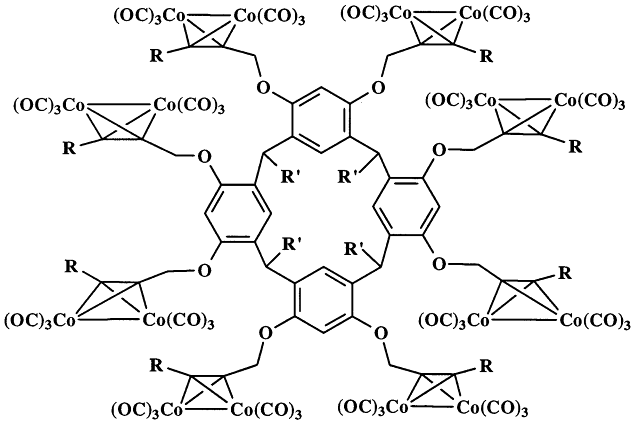


Figure 1. Side view of the structure of the octapropargyl resorcinarene derivative **2**. Note that two aryl groups are shown side-on; therefore, not all carbon atoms are visible. Selected bond distances (Å) and angles (deg): C(1A)−C(2A), 1.176(4); C(1A)−C(2A)−C(3A), 178.3(3); C(13A)−C(14A), 1.181(4); C(14A)−C(13A)−C(12A), 177.8(4).



9, **R = H;** 10, **R = Me**

In both **2** and **9**, the resorcinarene skeleton has approximate C_{2v} symmetry, thus defining a boat conformation with opposite pairs of resorcinol arene groups more "upright" and "flattened" than in a C_{4v} crown conformation.[2] The distortion from the crown conformation is driven by steric effects and is considerably greater in **9** than in **2**. The angle between the planes of the flattened rings is 148° in **9** compared to 140° in **2**, and the angle between the planes of the upright rings is 21° in **9** and 28° in **2**. Presumably the greater

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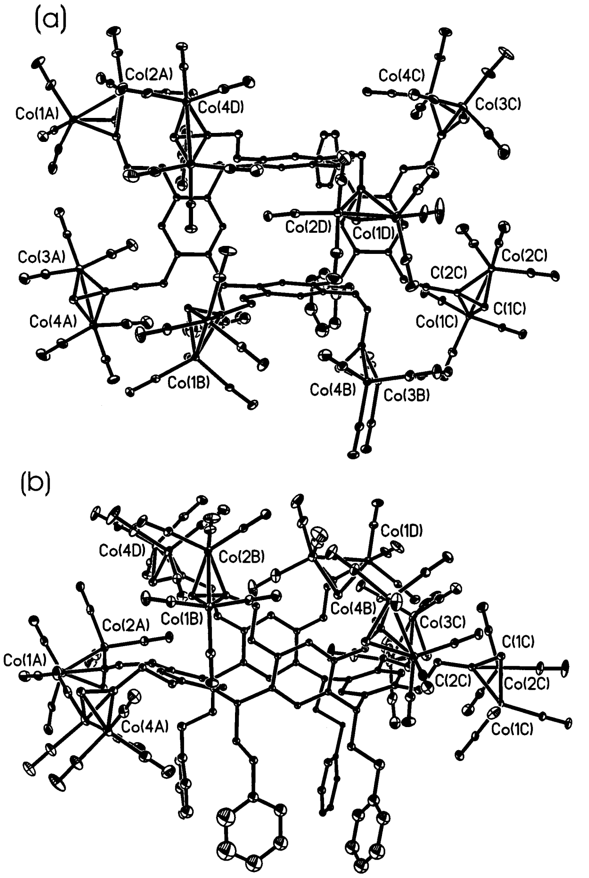
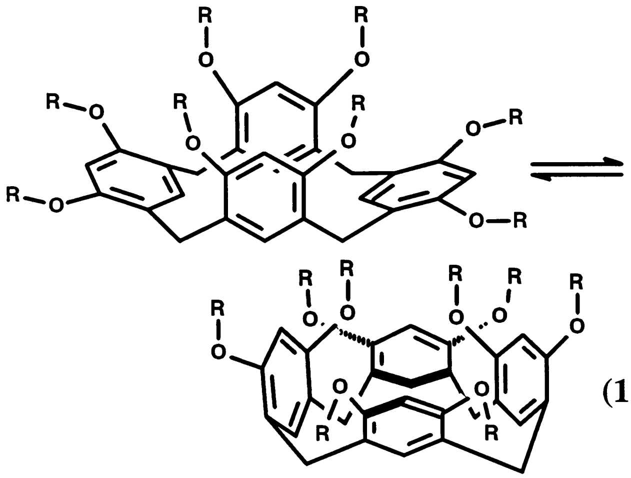


Figure 2. (a) Top view and (b) side view of the structure of the Co_{16} complex **9**. The steric congestion in the molecule is obvious. Selected bond distances (Å) and angles (deg): Co(1C)−Co(2C), 2.464(1); C(1C)−C(2C), 1.327(7); Co(1C)−C(1C), 1.962(5); Co(1C)−C(2C), 1.953(5); Co(2C)−C(1C), 1.949(5); Co(2C)−C(2C), 1.972(5); C(1C)−C(2C)−C(3C), 142.1(5).

deformation in **9** occurs to maximize the distance between the $Co_2(CO)_6$ groups and so to minimize steric hindrance. A partial structure of **10** was determined crystallographically, but the disorder of cobalt carbonyl groups and weak diffraction did not allow full refinement. The overall structure was similar to that of complex **9** (approximate C_{2v} symmetry, boat conformation).

The ^1H NMR spectra of compounds **2**−**5**, **9**, and **10** at room temperature indicate that they have effective C_{4v} symmetry, thus suggesting that easy interconversion between equivalent boat conformations occurs (eq 1). For example, only one set of aryl resonances for the resorcinol groups was observed, as expected if the upright and flattened aryl groups interconvert rapidly. The methylene protons of the propargyl arms are diastereotopic and thus appear as an AB multiplet ($J(H^aH^b)$ = 16 Hz in **2**), which is further split in **2** by coupling to the acetylenic proton. The peak for the acetylenic CCH protons of the propargyl groups is shifted considerably in the cobalt carbonyl derivative **9** (δ 6.1) compared to the parent octaalkyne **2** (δ 2.6), and this resonance is of course absent in the alkynyl complexes **4** and **5**.

For compound **2** the NMR spectra were essentially unchanged at −80 °C, indicating a low energy barrier for the fluxionality of eq 1,[2] but several resonances for **9** were broad at room temperature and they split at lower temperatures. At −20 °C, the ^1H spectrum of **9** is resolved, giving the spectrum expected for the boat conformation. Thus, two broad singlets were observed for each of the Ar protons, the acetylenic protons, and the methylene protons of the propargyl arms. These separate peaks correspond to the upright and flattened portions of the boat conformation of **9**. The resonances for each CH_2 group of the phenylethyl substituents (R′ in Chart 1) also split at −20 °C, as these protons are diastereotopic in the boat conformation. The ^{13}C NMR spectrum of complex **9** at −20 °C showed similar splittings. The coalescence temperature (T_c) of −15 °C for the methylene protons was used to determine the free energy of activation ($\Delta G^* = 51(1)$ kJ mol^{-1}) for the fluxionality according to eq 1, which is clearly considerably higher than for the parent compound **2**. Complex **10** behaved similarly to **9**, and at −20 °C, the expected spectrum for the boat conformation was observed. The coalescence temperature for the NMR resonances corresponding to the methylene protons of the butynyl arms was 10 °C, indicating a higher free energy of activation for the fluxionality of eq 1 for **10** ($\Delta G^* = 57(1)$ kJ mol^{-1}) compared to **9** ($\Delta G^* = 51(1)$ kJ mol^{-1}). This is presumed to be due to the higher steric hindrance in complex **10**.

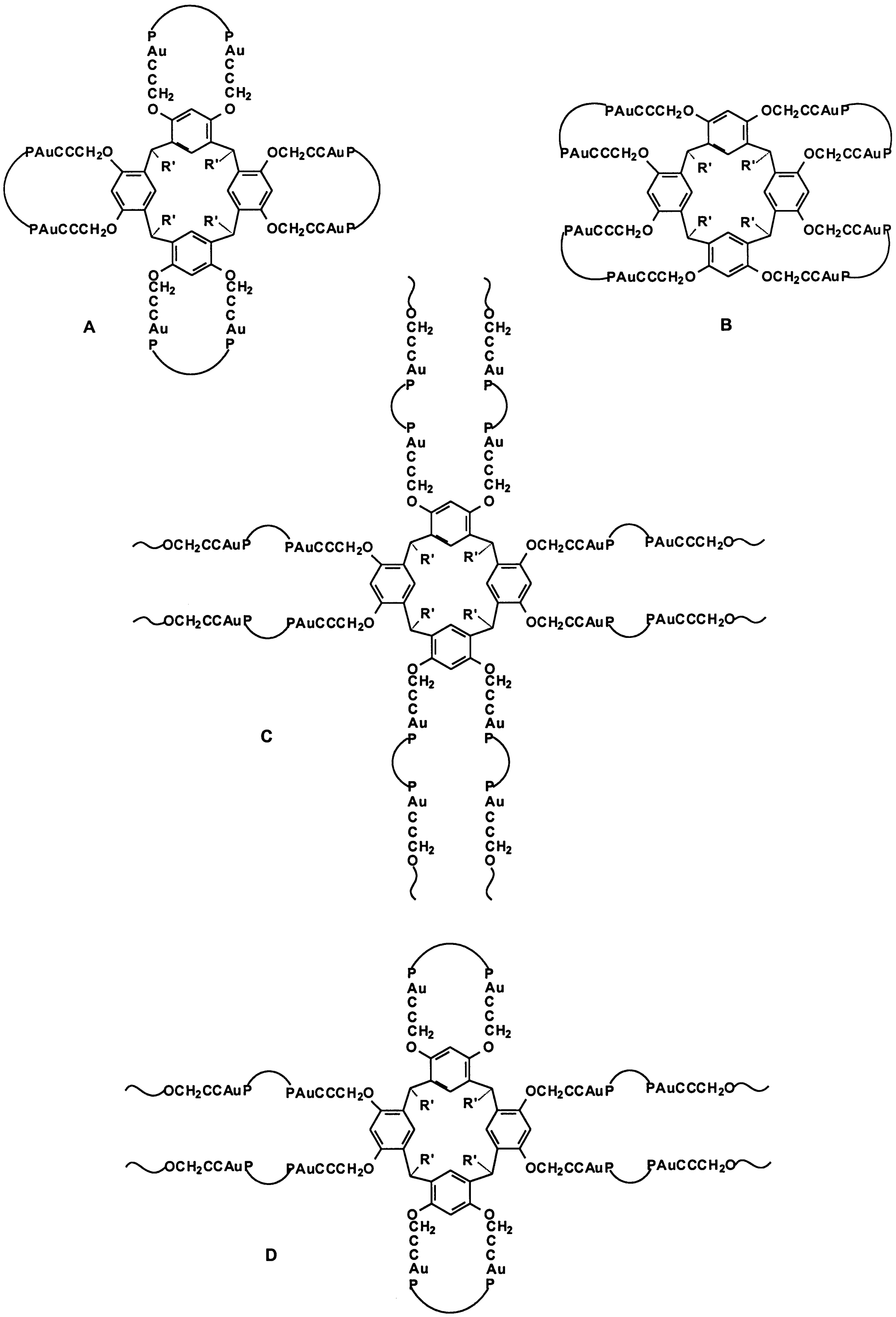


(1)

The ^1H NMR spectra of the alkynylgold(I) complexes **4** and **5** were similar to those of **2**, but without the CCH resonance. For complex **4**, a singlet was observed in the ^{31}P NMR spectrum, indicating effective equivalence of all (phosphine)gold(I) groups. The complex **4**, in which there are eight metal atoms that are well removed from the octopus center, exhibits easy fluxionality. The ^1H NMR resonances begin to split only at −60 °C, and the ^{31}P NMR resonance does not split down to −80 °C. The free energy of activation for the fluxionality of eq 1 (ΔG^* = 42(1) kJ mol^{-1}) is considerably lower than for complex **9** ($\Delta G^* = 51(1)$ kJ mol^{-1}).

The diphosphine complexes **6**−**8** were insoluble in all common organic solvents and thus could not be structurally characterized using NMR. The IR spectra of **6**−**8** confirmed the complete loss of the isocyanide ligands from the precursor complex **5**, and the composition of the products was confirmed by microanalytical data. Each diphosphine ligand will bridge two gold atoms in **6**−**8**,[11] and several structures are possible (Chart 2). The bridging could occur intramolecularly (**A** or **B**, Chart 2) or intermolecularly (**C**) or as a mixture of these two

Chart 2



motifs (for example, **D**, Chart 2). If the structure was **A** or **B**, or if the intermolecular bridges in **C** or **D** were between two bowls so as to make a dimeric “ball” structure (Chart 2), the complexes would be expected to be soluble; therefore, such structures are improbable.[12] It is more likely that polymeric structures such as **C** and **D** (Chart 2), with diphosphines bridging between gold atoms on different bowls, are formed.

Conclusions

In summary, this article describes the synthesis and structure of a complex with 16 cobalt atoms, the most metal atoms on a resorcinarene molecule, and the first structure determination of an “octopus” resorcinarene complex. The multiple metal substitution leads to much lower conformational flexibility of the resorcinarene in

9 compared to that of the parent **2** or less metalated derivative **4**.

Experimental Section

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. NMR and IR spectra were recorded using a Varian Inova 400 NMR or a Varian Inova 600 NMR and a Perkin-Elmer FT-IR 200 spectrometer, respectively. Resorcinarene **1** was prepared by the literature method.[9] Some of the compounds occlude solvent, which is partially lost on drying, and they give borderline acceptable analytical data.

Resorcinarene 2. A solution of **1** (7.15 g, 8 mmol) in acetone (250 mL) with K_2CO_3 (20 g) was treated with propargyl bromide (10.0 mL, 90 mmol) and refluxed for 24 h, followed by the addition of more propargyl bromide (10.0 mL, 90 mmol) and refluxing for another 24 h. The solvent was evaporated, and **2** was recrystallized from CH_2Cl_2/hexane. Yield: 9.0 g, 93%. NMR (CD_2Cl_2, 400 MHz): $\delta(^1H)$ 2.17 (m, 8H, $CHCH_2CH_2Ph$), 2.57 (m, 8H, OCH_2CCH), 2.59 (m, 8H, $CHCH_2CH_2Ph$), 4.53 (m, 16H, OCH_2CCH, $^2J_{HH} = 16$ Hz, $^4J_{HH} = 2$ Hz), 4.68 (t, 4H, $CHCH_2CH_2Ph$, $^3J_{HH} = 8$ Hz), 6.70 (s, 4H, Ar *H* ortho to O), 6.90 (s, 4H, Ar *H* meta to O), 7.14 (m, 20H, Ar *H*, $CHCH_2CH_2Ph$); $\delta(^{13}C)$ 34.52 ($CHCH_2CH_2Ph$) 35.03 ($CHCH_2CH_2Ph$), 38.11 ($CHCH_2CH_2Ph$), 57.34 (OCH_2CCH), 75.32 (OCH_2CCH), 79.74 (OCH_2CCH), 100.78 (Ar *C*H ortho to O), 126.41 (Ar *C*H meta to O), 127.75 (Ar*C*C ortho to O), 154.44 (Ar*C*O), 125.81, 128.53, 128.70, 143.18 (Ar *C*, $CHCH_2CH_2Ph$). FTIR: $\nu(C\equiv C)$ 2121 cm^{-1}. Anal. Calcd for **2**$\cdot CH_2Cl_2$ ($C_{85}H_{74}Cl_2O_8$): C, 78.9; H, 5.8. Found: C, 78.2; H, 5.7.

Resorcinarene 3. A solution of **1** (2 g, 2.2 mmol) in acetone (50 mL) with K_2CO_3 (5 g) was treated with 1-bromo-2-butyne (1.8 mL, 20.6 mmol) and refluxed for 24 h, followed by the addition of more 1-bromo-2-butyne (0.9 mL, 10.3 mmol) and refluxing for another 24 h. The solvent was evaporated, and **3** was recrystallized from CH_2Cl_2/hexane. Yield: 1.61 g, 55%. NMR (CD_2Cl_2, 400 MHz): $\delta(^1H)$ 1.90 (m, 24H, OCH_2CCCH_3), 2.15 (m, 8H, $CHCH_2CH_2Ph$), 2.59 (m, 8H, $CHCH_2CH_2Ph$), 4.50 (m, 16H, OCH_2CCCH_3), 4.66 (t, 4H, $CHCH_2CH_2Ph$, $^3J_{HH} = 8$ Hz), 6.68 (s, 4H, Ar *H* ortho to O), 6.88 (s, 4H, Ar *H* meta to O), 7.13 (m, 20H, Ar *H*, $CHCH_2CH_2Ph$); $\delta(^{13}C)$ 4.0 (CH_2CCCH_3), 34.83 ($CHCH_2CH_2Ph$), 35.26 ($CHCH_2CH_2Ph$), 38.54 ($CHCH_2CH_2Ph$), 58.18 (OCH_2CCCH_3), 75.45 (OCH_2CCCH_3), 83.40 (OCH_2CCCH_3), 100.86 (Ar *C*H ortho to O), 125.90 (Ar *C*C ortho to O), 126.42 (Ar *C*H meta to O), 154.93 (Ar*C*O), 127.51, 128.67, 128.89, 143.55 (Ar *C*, $CHCH_2CH_2Ph$). FTIR: $\nu(C\equiv C)$ 2241 cm^{-1}. Anal. Calcd for **3 (**$C_{92}H_{88}O_8$): C, 83.6; H, 6.7. Found: C, 84.2; H, 7.0.

Gold Complex 4. Complex **4** was prepared from **2** (0.13 g, 0.11 mmol) with $[AuCl(PPh_3)]$ (0.44 g, 0.88 mmol) and NaOAc (0.7 g) in THF/MeOH (10 mL/20 mL). Yield: 0.37 g, 69%. NMR in $CDCl_3$: $\delta(^1H)$ 2.14 (m, 8H, CH_2CH_2Ph), 2.64 (m, 8H, CH_2CH_2Ph), 4.71, 4.80 (m, 16H, $^2J(HH) = 15$ Hz, OCH_2CCAu), 4.85 (t, 4H, $^3J(HH) = 7$ Hz, $CHCH_2CH_2Ph$), 6.85 (s, 4H, Ar *H* ortho to O), 6.95 (s, 4H, Ar *H* meta to O), 7.0−7.6 (m, 140H, *Ph*); $\delta(^{31}P) = 42.5$ (s). FTIR: $\nu(C\equiv C)$ 2121 cm^{-1}. Anal. Calcd for $C_{228}H_{184}O_8P_8Au_8$: C, 56.2; H, 3.8. Found: C, 56.0; H, 3.9.

Gold Complex 5. A mixture of **2** (0.5 g, 0.41 mmol) and NaOAc (0.4 g) was stirred in THF/MeOH (25 mL/30 mL) and $AuCl(SMe_2)$ (0.950 g, 3.23 mmol) in THF/MeOH (40 mL/20 mL) was added dropwise over 5 min. This solution was stirred for 1.5 h, during which time a bright yellow precipitate formed. The solution was filtered and the solid washed with THF, MeOH, pentane (5 mL), and ether (50 mL). The solid was then suspended in CH_2Cl_2 (15 mL), *tert*-butyl isocyanide (0.4 mL, 3.54 mmol) was added, and the solution was stirred for 1 h. The yellow solution was concentrated and filtered through Celite, and then a yellow solid was precipitated with pentane. Yield: 0.6 g, 42%. NMR (CD_2Cl_2, 600 MHz): $\delta(^1H)$ 1.54 (s, 72H, $AuCNC(CH_3)_3$), 2.10 (m, 8H, $CHCH_2CH_2Ph$), 2.59 (m, 8H, $CHCH_2CH_2$ Ph), 4.62 (ABq, 16H, OCH_2CCAu, $^2J_{HH} = 16$ Hz), 4.63 (t, 4H, $CHCH_2CH_2Ph$, $^3J_{HH} = 8$ Hz), 6.79 (s, 4H, Ar *H* meta to O), 6.85 (s, 4H, Ar *H* ortho to O), 7.09 (m, 20H, Ar *H*, $CHCH_2CH_2Ph$); $\delta(^{13}C)$ 29.89 ($AuCNC(CH_3)_3$), 34.86 ($CHCH_2CH_2Ph$), 35.30 ($CHCH_2CH_2Ph$), 38.45 ($CHCH_2CH_2Ph$), 58.66 (OCH_2CCAu), 58.83 ($AuCNC(CH_3)_3$), 98.87 (OCH_2CCAu), 101.43 (Ar *C*H ortho to O), 119.62 (OCH_2CCAu), 125.77 (Ar *C*H meta to O), 126.69 (Ar *C*C ortho to O), 147.27 ($AuCNC(CH_3)_3$), 154.87 (Ar*C*O), 125.32, 128.33, 128.89, 143.96 (Ar *C*, $CHCH_2CH_2Ph$). FTIR $\nu(C\equiv C)$ 2143 cm^{-1}; $\nu(C\equiv N)$ 2226 cm^{-1}. Anal. Calcd for **5** ($C_{124}H_{136}O_8Au_8N_8$): C, 43.3; H, 4.0. Found: C, 43.9; H, 4.0.

Gold Complex 6. Complex **6** was prepared from **5** (0.1 g, 0.029 mmol) and bis(diphenylphosphino)methane (0.047 g, 0.119 mmol) in CH_2Cl_2 (10 mL). A white precipitate immediately formed, and the reaction mixture was stirred for 0.5 h. The solid was filtered and washed with THF, MeOH, and ether (10 mL). Yield: 0.114 g, 91%. FTIR: $\nu(C\equiv C)$ 2145 cm^{-1}. Anal. Calcd for **5** ($C_{184}H_{152}O_8Au_8P_8$): C, 51.2; H, 3.6. Found: C, 50.8; H, 3.5.

Gold Complex 7. Complex **7** was prepared from **5** (0.1 g, 0.029 mmol) and 1,2-bis(diphenylphosphino)ethane (0.047 g, 0.118 mmol) in CH_2Cl_2 (10 mL). A white precipitate immediately formed, and the reaction mixture was stirred for 0.5 h. The solid was filtered and washed with THF, MeOH, and ether (10 mL). Yield: 0.108 g, 85%. FTIR: $\nu(C\equiv C)$ 2148 cm^{-1}. Anal. Calcd for **5** ($C_{188}H_{160}O_8Au_8P_8$): C, 51.7; H, 3.7. Found: C, 51.2; H, 3.8.

Gold Complex 8. Complex **8** was prepared from **5** (0.1 g, 0.029 mmol) and 1,4-bis(diphenylphosphino)butane (0.052 g, 0.119 mmol) in CH_2Cl_2 (10 mL). A white precipitate immediately formed, and the reaction mixture was stirred for 0.5 h. The solid was filtered and washed with THF, MeOH, and ether (10 mL). Yield: 0.122 g, 91%. FTIR: $\nu(C\equiv C)$ 2146 cm^{-1}. Anal. Calcd for **5** ($C_{196}H_{176}O_8Au_8P_8$): C, 52.5; H, 4.0. Found: C, 52.9; H, 4.1.

Cobalt Complex 9. Complex **9** was prepared from **2** (0.186 g, 0.15 mmol) and $Co_2(CO)_8$ (0.585 g, 1.71 mmol) in CH_2Cl_2 (10 mL) under nitrogen for 16 h and purified by chromatography on silica gel, with CH_2Cl_2/hexane (1:9) as eluent. The first dark red band was **9**, which was recrystallized from CH_2Cl_2/hexane. Yield: 27%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.17 (m, 8H, $CHCH_2CH_2Ph$), 2.53 (m, 8H, $CHCH_2CH_2Ph$), 4.91 (t, 4H, $CHCH_2CH_2Ph$, $^3J_{HH} = 7$ Hz), 5.22 (s, 16H, OCH_2CCH), 6.10 (s, 8H, OCH_2CCH), 6.61 (s, 4H, Ar *H* ortho to O), 7.0 (s, 4H, Ar *H* meta to O), 7.06 (m, 20H, Ar *H* $CHCH_2CH_2Ph$); $\delta(^{13}C)$ 34.59 ($CHCH_2CH_2Ph$), 35.34 ($CHCH_2CH_2Ph$), 38.77 ($CHCH_2CH_2Ph$), 70.27 (br, OCH_2CCH), 73.94 (OCH_2CCH), 89.33 (OCH_2CCH), 100.33 (Ar *C*H ortho to O), 125.80 (Ar *C*C ortho to O), 127.80 (Ar *C*H meta to O), 155.01 (Ar *C*O), 128.30, 128.57, 128.60, 143.21 (Ar *C* $CHCH_2CH_2Ph$), 199.77 ($Co_2(CO)_6$). NMR (CD_2Cl_2, 600 MHz, −20 °C): $\delta(^1H)$ 2.06, 2.10 (s, 8H, $CHCH_2CH_2Ph$), 2.31, 2.57 (s, 8H, $CHCH_2CH_2Ph$), 4.84 (s, 4H, $CHCH_2CH_2Ph$), 5.11, 5.40 (s, 16H, OCH_2CCH), 5.90, 6.25 (s, 8H, CH_2CCH), 6.39, 6.69 (s, 4H, Ar *H* ortho to O), 7.51, 6.53 (s, 4H, Ar *H* meta to O), 7.03 (m, 20H, Ar *H* $CHCH_2CH_2Ph$); $\delta(^{13}C)$ 34.12 ($CHCH_2CH_2Ph$), 34.36 ($CHCH_2CH_2Ph$), 39.10 ($CHCH_2CH_2Ph$), 68.30, 70.57 (OCH_2CCH), 73.56, 74.09 (OCH_2CCH), 87.83, 89.26 (OCH_2CCH), 98.37, 99.22 (Ar *C*H ortho to O),124.22, 125.50 (Ar *C*C ortho to O), 127.32 (br, Ar *C*H meta to O), 154.19, 154.30 (Ar *C*O), 128.29, 128.31, 142.97 (Ar *C* $CHCH_2CH_2Ph$), 199.36, 199.69 ($Co_2(CO)_6$). FTIR: $\nu(CO)$ 2098, 2054, 2025 cm^{-1}. Anal. Calcd for **9**·(hexane) ($C_{138}H_{86}O_{56}Co_{16}$): C, 46.3; H, 2.4. Found: C, 46.0; H, 2.0.

Cobalt Complex 10. Complex **10** was prepared by reaction of **3** (0.2 g, 0.15 mmol) with $Co_2(CO)_8$ (0.5 g, 1.46 mmol) in CH_2Cl_2 (10 mL) under N_2 for 2 h and purified by chromatography on silica gel, with CH_2Cl_2/hexane(2:3) eluent. The first dark red band was **10**, which was recrystallized from CH_2Cl_2/hexane. Yield: 0.380 g, 70%. NMR (CD_2Cl_2, 400 MHz): $\delta(^1H)$ 2.17 (m, 8H, $CHCH_2CH_2Ph$), 2.49 (br, 32H, $CHCH_2CH_2Ph$, OCH_2CCCH_3), 4.94 (t, 4H, $CHCH_2CH_2Ph$, $^3J_{HH}$

= 8 Hz), 5.25 (br, 16H, OC*H*$_2$CCCH$_3$), 6.66 (br, 6H, Ar *H*), 7.10 (m, 20H, CHCH$_2$CH$_2$*Ph*), 7.10 (br, 2H, Ar *H*); δ(^{13}C) 20.96 (OCH$_2$CC*C*H$_3$), 34.75 (CH*C*H$_2$CH$_2$Ph), 35.68 (*C*HCH$_2$CH$_2$Ph), 39.15 (CHCH$_2$*C*H$_2$Ph), 70.29 (br, O*C*H$_2$CCCH$_3$), 91.55, 94.95 (OCH$_2$*CC*CH$_3$), 99.76 (Ar *C*H ortho to O), 155.41 (Ar *C*O), 125.89, 128.65, 143.27 (Ar *C*C ortho to O, Ar *C*H meta to O, Ar *C* CHCH$_2$CH$_2$*Ph*), 200.18 (Co$_2$(*C*O)$_6$). NMR (CD$_2$Cl$_2$, 400 MHz, −20 °C): δ(^{1}H) 2.12 (s, 8H, CHC*H*$_2$CH$_2$Ph), 2.31 (br, 16H, CHCH$_2$C*H*$_2$Ph, OCH$_2$CCC*H*$_3$), 2.56 (s, 4H, CHCH$_2$C*H*$_2$Ph), 2.67 (s, 12H, OCH$_2$CCC*H*$_3$), 4.92 (t, C*H*CH$_2$CH$_2$Ph, $^3J_{\mathrm{HH}}$ = 8 Hz), 5.16, 5.34 (m, 16H, OC*H*$_2$CCCH$_3$), 6.40, 6.63, 6.69, 7.58 (s, 8H, Ar *H*), 6.98 (m, Ar *H* CHCH$_2$CH$_2$*Ph*). FTIR: ν(CO) 2093, 2053, 2019 cm^{-1}. Anal. Calcd for **10**·CH$_2$Cl$_2$ (C$_{141}$H$_{90}$O$_{56}$Co$_{16}$Cl$_2$): C, 45.9; H, 2.5. Found: C, 46.0; H, 2.6.

X-ray Structure Determinations. A crystal was mounted on a glass fiber. Data were collected using a Nonius-Kappa CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The SHELXTL (G. M. Sheldrick, Madison, WI) program package was used to solve and refine the structure. The hydrogen atoms were calculated geometrically riding on their respective carbon atoms. Crystal data are summarized in Table 1.

Resorcinarene 2. Crystals of [C$_{84}$H$_{72}$O$_8$]·CH$_2$Cl$_2$ were grown from slow diffusion of hexane into a dichloromethane solution. One of the CH$_2$CCH arms (C12B−C14B) was disordered and was modeled as two isotropic components with 50% occupancy. The dichloromethane solvate was also disordered and was modeled as a 60/40 mixture, with anisotropic heavy atoms but with the C−Cl distance fixed at 1.65 Å. Except as noted above, the non-hydrogen atoms were refined with anisotropic thermal parameters. The largest residual electron density peak (0.199 e/Å^3) was associated with one of the hydrogen atoms, H10A.

Cobalt Complex 9. Crystals of [C$_{132}$H$_{72}$O$_{56}$Co$_{16}$]·(hexane) were grown from slow diffusion of hexane into a dichloromethane solution. One of the Co$_2$(CO)$_6$ groups was disordered and was modeled as a 60/40 mixture. The Co−C distances were constrained to be equal and refined. The C−O distances of the carbonyl groups were treated similarly. One of the dangling phenyl rings was modeled as a mixture of two half-occupancy groups. All the cobalt atoms and carbonyl groups were refined anisotropically. The remainder of the molecule was refined isotropically. The hexane of solvation was modeled ideally with C−C and C(C)C distances of 1.54 and 2.51 Å. The largest residual electron density peak (1.591 e/Å^3) was associated with one of the carbon atoms, C12C.

Table 1. Crystallographic Data for 2 and 9

	2·CH$_2$Cl$_2$	**9**·(hexane)
empirical formula	C$_{85}$H$_{74}$Cl$_2$O$_8$	C$_{138}$H$_{86}$Co$_{16}$O$_{56}$
fw	1294.34	3582.95
temp (K)	200(2)	150(2)
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.1933(11)	15.0144(3)
b (Å)	13.2660(12)	19.7712(3)
c (Å)	22.6061(17)	25.3065(4)
α (deg)	103.860(4)	97.949(1)
β (deg)	94.265(4)	94.938(1)
γ (deg)	110.581(4)	96.814(1)
V (Å^3)	3541.0(5)	7351.2(2)
Z	2	2
d_{calcd} (Mg/m^3)	1.214	1.619
abs coeff (mm^{-1})	0.149	1.840
F(000)	1364	3588
cryst size (mm)	0.51 × 0.34 × 0.29	0.30 × 0.30 × 0.20
range for data collection (deg)	2.15−23.24	2.64−27.52
R1, wR2 ($I > 2\sigma$)	0.0501, 0.1139	0.0742, 0.1819
largest diff peak and hole (e Å^{-3})	0.199 and −0.266	1.591 and −1.027

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Supporting Information Available: Tables giving X-ray data for compounds **2** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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