An Organometallic Methodology Affording Dinuclear Copper(I) Complexes

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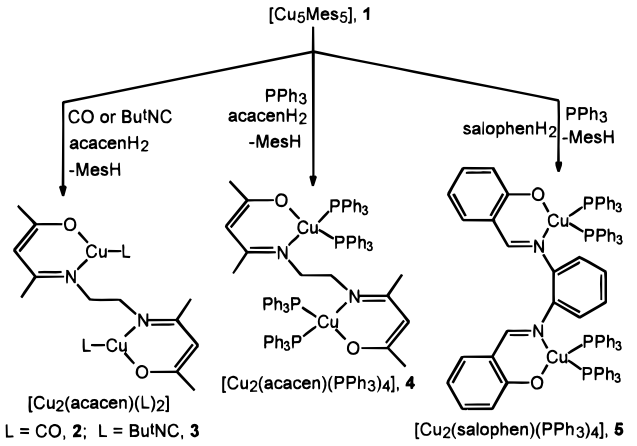
Introduction

Synthetic access to the very important class of copper(I) coordination compounds is based on the metathesis reaction between copper halides and the salt of the corresponding ligand.[1−3] Such reactions must be carried out in coordinating polar solvents, which is usually why copper(I) disproportionates to copper(II) and copper metal. An additional problem, mainly when we are dealing with a polynucleating polyprotic ligand, can be the difficulty in obtaining the ligand as the alkali metal salt and in managing the nuclearity of the resulting compound. Thus we felt the necessity for a different metalating methodology in the case of copper(I) complexes, which should avoid the use of any salt and halide derivative, that is, the direct reaction of a copper(I) source with the protic form of the ligand in an innocent solvent. This method employing $[Cu_5Mes_5]$[4] [Mes = 2,4,6-$Me_3C_6H_2$] as starting material has been efficiently used in organometallic chemistry by van Koten and co-workers.[5] We wish to illustrate the effectiveness of such a method in the synthesis of dinuclear copper(I) complexes,[6,7] which are particularly attractive, and, among others, in the field of dioxygen activation.[6,7] In order to emphasize the relevance of this synthetic approach, we used molecules which are usually mononucleating ligands but are potential binucleating ligands, such as the tetradentate Schiff bases, which can force two copper(I) ions into an interesting close geometrical proximity. These ligands, used under conventional conditions, induce the disproportionation of copper(I).[2] We report here the reaction of the homoleptic copper(I)−aryl $[Cu_5Mes_5]$ compound, which is available on a large scale,[4] with acacenH_2 [*N*,*N*′-ethylenebis(acetylacetone imine)], salophenH_2 [*N*,*N*′-*o*-phenylenebis(salicylaldimine)], and *o*-phthalic acid, leading to a variety of dinuclear copper(I) complexes.

Scheme 1



Results and Discussion

The metalation of tetradentate Schiff bases, such as acacenH_2 [*N*,*N*′-ethylenebis(acetylacetone imine)] and salophenH_2 [*N*,*N*′-*o*-phenylenebis(salicylaldimine)], in their protic forms was carried out by mixing either toluene or THF solutions of $[Cu_5Mes_5]$, **1** (Mes = 2,4,6-$Me_3C_6H_2$), and the ligand in the presence of a copper(I)-stabilizing agent such as CO, PPh_3, RNC.[2] The metalation of acacenH_2 and salophenH_2 is reported in Scheme 1.

The *trans* arrangement of the halves of such ligands, which normally act as tetradentate binders for a single metal ion, is based on the X-ray-determined solid state structure of **4**. We should comment, however, that we are referring to the solid state, while in solution the *cis* arrangement may also be possible and the two metal centers may be accessible in the appropriate disposition for dinuclear reactivity. In the case of complex **2**, the reaction was also carried out in a carbon monoxide atmosphere. Although CO loss from the solid is facile, it rebinds under such conditions. The CO stretching vibration for **2** is very high (2071 cm^{-1}),[8] in agreement with the electrophilic nature of the d^{10} metal which is unable to π-back-donate. Compound **3** shows the same spectroscopic characteristics as **2**, with a very high stretching vibration of the C≡NR group at 2166 cm^{-1}, though in the latter case there is no reversibile binding of ButNC, as in the case of carbon monoxide.[8] On the

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(1) (a) *Copper Coordination Chemistry: Biochemistry and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983. (b) *Biological and Inorganic Copper Chemistry;* Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1986.
(2) Hataway, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 533.
(3) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.
(4) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.
(5) (a) Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1252−1253. (b) Aalten, H. L.; van Koten, G.; Riethorst, E.; Stam, C. H. *Inorg. Chem.* **1989**, *28*, 4140−4146. (c) Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *Organometallics* **1989**, *8*, 2293−2299. (d) van Koten, G.; Stuart, L. J.; Jastrzebski, J. T. B. H. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 3, Chapter 2.
(6) Kitajima, K.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737 and references therein.
(7) Wei, N.; Lee, D. H.; Murthy, N. N.; Tyeklar, Z.; Karlin, K. D.; Kaderli, S.; Jung, B.; Zuberbuehler, A. D. *Inorg. Chem.* **1994**, *33*, 4625. Karlin, K. D.; Nasir, M. S.; Cohen, B. I.; Cruse, R. W.; Kaderli, S.; Zuberbuehler, A. D. *J. Am. Chem. Soc.* **1994**, *116*, 1324. Wei, N.; Murthy, N. N.; Tyeklar, Z.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1177. Sanyal, I.; Karlin, K. D.; Strange, R. W.; Blackburn, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 11259. Karlin, K. D.; Tyeklar, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Toscano, P. J.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 1436. Sanyal, I.; Mahroof-Tahir, M.; Nasir, M. S.; Ghosh, P.; Cohen, B. I.; Gultneh, Y.; Cruse, R. W.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 4322. Mahroof, T. M.; Karlin, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 7599. Paul, P. P.; Tyeklar, Z.; Jacobson, R. R.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 5322. Sanyal, I.; Strange, R. W.; Blackburn, N. J.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 4692. Tyeklar, Z.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 388. Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196. Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668.
(8) Pasquali, M.; Floriani, C. Copper(I)-Carbon Monoxide Chemistry: Recent Advances and Perspectives. In Ref 1a, pp 311−330.

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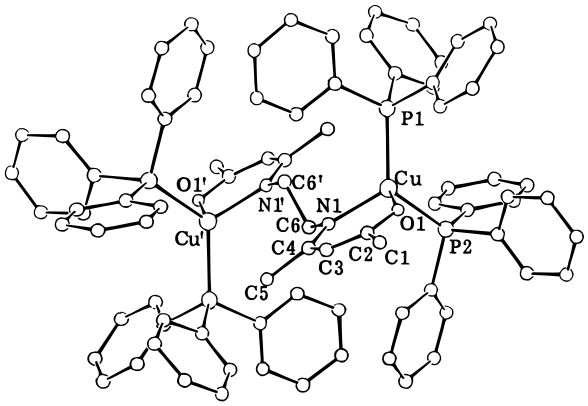


Figure 1. SCHAKAL drawing of complex **4**. Prime indicates a transformation of $1 - x, -y, -z$.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **4**

Cu−P1	2.258(1)	N1−C6	1.467(7)
Cu−P2	2.277(1)	C1−C2	1.517(8)
Cu−O1	2.038(4)	C2−C3	1.368(8)
Cu−N1	2.019(4)	C3−C4	1.422(8)
O1−C2	1.275(6)	C4−C5	1.510(9)
N1−C4	1.301(6)	C6−C6′	1.518(8)
O1−Cu−N1	94.2(2)	P1−Cu−P2	123.5(1)
P2−Cu−N1	108.1(1)	Cu−O1−C2	122.0(4)
P2−Cu−O1	101.3(1)	Cu−N1−C6	117.2(3)
P1−Cu−N1	119.8(1)	Cu−N1−C4	123.2(4)
P1−Cu−O1	103.1(1)		

other hand, the kinetic lability of CO makes **2** particularly appropriate for reactivity studies. In case of PPh_3, we have an overstabilization of copper(I), achieving tetracoordination in both **4** and **5**. The major difference between the two stays in the approximately juxtaposition of the two copper(I) centers in the possible cisoid arrangement. The centrosymmetric structure of complex **4** is shown in Figure 1, and a selection of bond distances and angles is given in Table 1. The structural parameters are in the usual range for both the coordination sphere[1] and the ligand acacen,[9] are quite close to what we found in dinuclear copper(I)−CO and copper(I)−CNR complexes containing the *N*,*N*′-ethylenebis(benzaldimine) ligand,[10] and are not affected by the *trans* arrangement of the halves of the ligand.

The reactions in Scheme 1 should lead to the disproportionation of copper(I). This is not observed for two reasons: the nature of the solvent (*i.e.* toluene) and the auxiliary ligands (*i.e.* CO, PPh_3, and Bu^tNC).[1] Such ligands function to stabilize copper(I) and greatly enhance the solubility of the resulting complexes. Even in the absence of such ligands, in non-strongly-coordinating solvents we obtained dinuclear copper(I) complexes which, however, disproportionate in protic solvents, such as methanol. An unprotected copper(I) dinuclear complex has been isolated and used in further synthesis (see Scheme 2).

The copper carboxylate **6** made by this method is stable even in the absence of a stabilizing agent, which can be added in a subsequent step.[11] This methodology has been previously successfully applied to the synthesis of monocarboxylato copper-

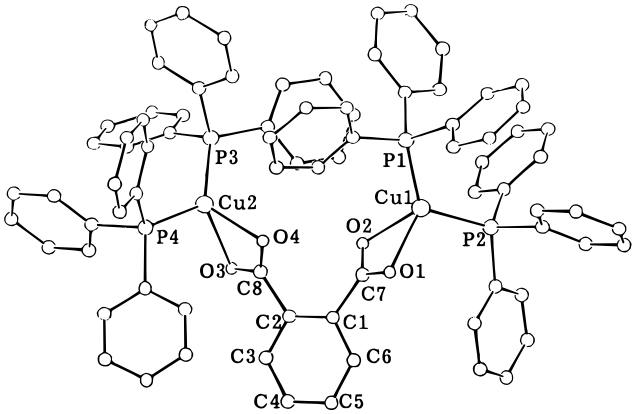
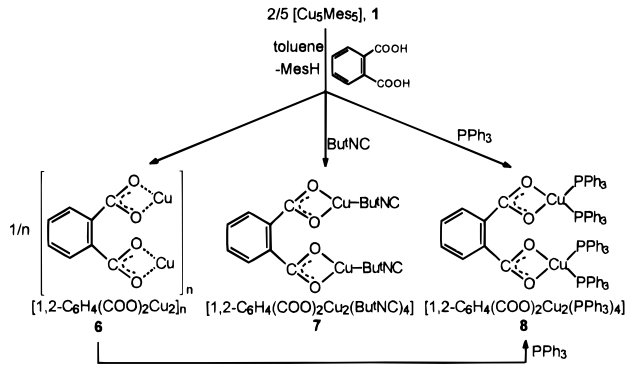


Figure 2. SCHAKAL drawing of complex **8**.

Scheme 2



(I) derivatives by van Koten.[5] The polymeric form **6**, which is quite insoluble, dissolves in the presence of auxiliary ligands; thus **6** can be a source of an appropriate dinuclear skeleton. Copper(I) becomes three-coordinate in **7** and tetracoordinate in **8**, as in Scheme 1. We should mention that carboxylate ligands are among the most interesting starting materials in copper(I) chemistry and oligomeric stable forms derived from monocarboxylic acids are well-known.[5,11] The proposed dinuclear skeleton shown for **6**−**8** is based on the X-ray analysis of **8**, shown in Figure 2. In complex **8**, the bidentate bonding mode of the carbocylato anions is nonsymmetric with significant differences between Cu1−O1 (oxy) and Cu1−O2 and between Cu2−O3 and Cu2−O4 (see Table 2). There is an additional difference in the Cu−O environment between Cu1 and Cu2. All these parameters are in agreement with those found in a series of copper(I) carboxylato derivatives.[5,11] The Cu1···Cu2 distance [6.241(2) Å] may be appropriate for the interaction of the dinuclear unit with a single substrate.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. The NMR spectra were recorded on a 200-AC instrument.

Preparation of 2. Solid **1** (1.28 g, 7.03 mmol) was added to a THF (100 mL) solution of acacenH_2 (0.79 g, 3.52 mmol) cooled to −20 °C.

(9) Mazzanti, M.; Rosset, J.-M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 953. Corazza, F.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1335. Solari, E.; Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1345. Rosset, J.-M.; Floriani, C.; Mazzanti, M.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1990**, *29*, 3991. Gallo, E.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 2156.

(10) Toth, A.; Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 648.

(11) (a) Pasquali, M.; Leoni, P.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1982**, *21*, 4324. (b) Toth, A.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1987**, *26*, 236. (c) Lockhart, T. P.; Haito, D. A. *Polyhedron* **1985**, *4*, 1745. (d) Lijima, K.; Itoh, T.; Shibata, S. *J. Chem. Soc., Dalton Trans.* **1985**, 2555. (e) Rodesiler, P. F.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1974**, 599. (f) Mounts, R. D.; Ogura, T.; Fernando, Q. *Inorg. Chem.* **1974**, *13*, 802. (g) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1977**, 299. (h) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Chem. Commun.* **1973**, 124. (i) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2463.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **8**

Cu1−P1	2.236(4)	Cu2−P3	2.229(4)
Cu1−P2	2.248(4)	Cu2−P4	2.246(4)
Cu1−O1	2.268(9)	Cu2−O3	2.350(10)
Cu1−O2	2.140(9)	Cu2−O4	2.092(9)
O1−C7	1.258(18)	O3−C8	1.245(18)
O2−C7	1.246(17)	O4−C8	1.256(18)
C1−C7	1.504(16)	C2−C8	1.503(16)
O2−Cu1−C7	29.5(4)	O4−Cu2−C8	29.5(4)
O1−Cu1−C7	29.8(4)	O3−Cu2−C8	29.1(4)
O1−Cu1−O2	59.3(3)	O3−Cu2−O4	58.5(4)
P2−Cu1−C7	112.4(3)	P4−Cu2−C8	109.4(4)
P2−Cu1−O2	111.8(3)	P4−Cu2−O4	108.4(3)
P2−Cu1−O1	108.9(3)	P4−Cu2−O3	108.2(3)
P1−Cu1−C7	122.5(3)	P3−Cu2−C8	123.0(4)
P1−Cu1−O2	117.6(3)	P3−Cu2−O4	121.4(3)
P1−Cu1−O1	116.2(3)	P3−Cu2−O3	112.8(3)
P1−Cu1−P2	124.9(2)	P3−Cu2−P4	126.7(2)
Cu1−O1−C7	86.6(8)	Cu2−O3−C8	84.0(9)
Cu1−O2−C7	92.8(8)	Cu2−O4−C8	95.6(8)

After complete dissolution of the solid, the solution was saturated with CO while being stirred and a progressive darkening of the yellow color observed. The solution was then cooled to −30 °C and kept at this temperature for 5 days. Colorless thin needles formed, which, after filtration, became yellowish. After 30 min of drying (oil pump), the product was completely yellow but became colorless again when exposed to a CO atmosphere (44%). Anal. Calcd for $C_{14}H_{18}Cu_2N_2O_4$: C, 41.48; H, 4.48; N, 6.91. Found: C, 41.36; H, 4.50; N, 6.95. ^{1}H NMR (200 MHz, CD_2Cl_2, 298 K, ppm): δ 4.93 (s, 2 H), 3.76 (s, 2 H), 3.76 (s, 4 H), 1.94 (m, 12 H). IR (Nujol): ν(CO) 2071 cm^{-1}.

Preparation of 3. Solid **1** (1.42 g, 1.42 mmol) was added to a THF (100 mL) solution of acacenH_2 (0.87 g, 3.28 mmol) cooled to −20 °C. After complete dissolution of the solid, Bu^{t}NC was added *via* syringe. Thin white needles formed suddenly, which were filtered off and dried (55%). Anal. Calcd for $C_{22}H_{36}Cu_2N_4O_2$: C, 51.25; H, 7.04; N, 10.86. Found: C, 51.40; H, 6.98; N, 10.84. IR (Nujol): ν(C≡N) 2166 cm^{-1}.

Preparation of 4. Addition of a solution of acacenH_2 (0.57 g, 2.56 mmol) and PPh_3 (2.69 g, 10.25 mmol) in toluene (100 mL) to a toluene (100 mL) solution of **1** (0.94 g, 5.12 mmol) resulted in a bright-yellow solution which under stirring turned to opalescent-white. Standing for 24 h at room temperature gave translucent crystals, which were filtered off. The mother liquor was concentrated and cooled to +4 °C. After 1 week, more crystals formed (38%). Anal. Calcd for $C_{84}H_{78}Cu_2N_2O_2P$: C, 72.14; H, 5.62; N, 2.00; P, 8.86. Found: C, 72.36; H, 5.74; N, 1.88; P, 8.64. ^{1}H NMR (200 MHz, CD_2Cl_2, room temperature, ppm): δ 7.35 (m, 30 H), 4.68 (s, 2 H), 3.41 (s, 4 H), 1.93 (s, 6 H), 1.41 (s, 6 H).

Preparation of 5. Addition of a solution of salophenH_2 (0.70 g, 2.22 mmol) and PPh_3 (2.33 g, 8.88 mmol) in toluene (100 mL) to a toluene (100 mL) solution of **1** (0.81 g, 4.44 mmol) resulted in a yellow solution which turned bright-orange as the reaction proceeded. After some minutes of stirring, an orange microcrystalline solid formed, which was filtered off and dried for 2 h *in vacuo* (68%). The product was air stable. Anal. Calcd for $C_{92}H_{74}Cu_2N_2O_2P_4$: C, 74.13; H, 5.00; N, 1.88; P, 8.31. Found: C, 74.10; H, 4.86; N, 6.98; P, 8.19. ^{1}H NMR (200 MHz, CD_2Cl_2, 298 K, ppm): δ 7.30 (m, 72 H), 7.60 (m, 2 H).

Preparation of 6. To a solution of **1** (0.74 g, 4.05 mmol) in toluene (100 mL) was added *o*-phthalic acid (0.34 g, 2.05 mmol). The reaction was slow, due to the low solubility of the *o*-phthalic acid in the reaction solvent. After 12 h of stirring, an amorphous light-yellow solid was collected and dried for 2 h *in vacuo* (65%). Anal. Calcd for $C_8H_4Cu_2O_4$: C, 33.00; H, 1.38. Found: C, 33.01; H, 1.52.

Preparation of 7. To a stirred toluene (100 mL) solution of **1** (0.74 g, 4.23 mmol) was added *o*-phthalic acid (0.35 g, 2.11 mmol), and the resulting yellow suspension was stirred for 12 h, after which Bu^{t}NC (0,50 mL, 4.42 mmol) was added *via* syringe. The suspended solid dissolved, and after 5 min, a white microcrystalline solid precipitated, which was filtered off and dried (85%). IR (Nujol): ν(C≡N) 2168 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2, 298 K, ppm): δ 7.60 (m, 2 H), 7.30 (m, 2 H), 1.41 (s, 18 H).

Table 3. Experimental Data for the X-ray Diffraction Studies of Complexes **4** and **8**[a]

	4	**8**
empirical formula	$C_{84}H_{78}Cu_2N_2O_2P_4 \cdot C_7H_8$	$C_{80}H_{64}Cu_2O_4P_4 \cdot C_7H_8$
M_r	1490.7	1432.5
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
cell params at 295 K[b]		
a, Å	18.612(2)	12.253(1)
b, Å	14.341(1)	22.403(2)
c, Å	14.840(1)	26.696(2)
β, deg	99.05(1)	98.68(1)
V, Å^3	3911.7(6)	7244.2(11)
Z	2	4
D_{calcd}, g cm^{-3}	1.266	1.313
F(000)	1560	2976
linear abs coeff, cm^{-1}	6.73	7.25
cryst dimens, mm	0.37 × 0.64 × 0.67	0.32 × 0.51 × 0.55
2θ range, deg	6−46	6−46
no. of unique total data	5508	9225
no. of unique obsd data	3452	3248
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.048	0.060
$R = \sum w^{1/2}\|\Delta F\|/\sum w^{1/2}\|F_o\|$	0.052	
GOF $= \sum w\|\Delta F\|^2/(NO - NV)]^{1/2}$	0.85	

[a] Details pertaining to both complexes: Philips PW 1100 diffractomter; $\omega/2\theta$ scan type; monochromated Mo Kα radiation (λ = 0.710 69 Å); criterion for observation $I > 2\sigma(I)$. [b] Unit cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centered reflections chosen from diverse regions of reciprocal space.

Preparation of 8. Addition of **6** (0.25 g, 0.86 mmol) to a stirred solution of PPh_3 (0.91 g, 3.47 mmol) in toluene (100 mL) resulted in a solution, which was then left at −30 °C for 10 days. Translucent crystals were collected (66%). Anal. Calcd for $C_{80}H_{64}Cu_2O_4P_4$: C, 71.69; H, 4.81; P, 9.24. Found: C, 73.35; H, 5.17; P, 8.22. ^{1}H NMR (200 MHz, CD_2Cl_2, 298 K, ppm): δ 7.25 (m, 64 H).

X-ray Diffraction Study of 4 and 8. Crystal data and details associated with data collection and refinement are given in Table 3. The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected. The structures were solved by the heavy-atom method (Patterson and Fourier techniques). For complex **4**, refinement was done first isotropically and then anisotropically for all the non-hydrogen atoms except for those of the toluene solvent molecule, which was found to be disordered about a center of symmetry. For complex **8**, all atoms except the phosphine phenyl carbons and the toluene solvent carbons were allowed to vary anisotropically. For both structures, all the Ph rings were constrained to be regular hexagons (C−C = 1.395 Å). All H atoms were put in calculated positions and introduced in refinement as fixed contributors with isotropic U values fixed at 0.08 Å^2.

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-40268.94) for financial support.

Supporting Information Available: Tables of fractional atomic coordinates, thermal parameters, and complete interatomic distances and angles for **4** and **8** (11 pages). Ordering information is given on any current masthead page.

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