rapid metal exchange between the two nitrogen atoms. Computer simulation of the line shapes at various temperatures (illustrated in Figure 1 for M = Cr, line width 1.5 Hz) leads to the thermodynamic parameters listed in Table I by use of the same method as was described above for the phth complexes. The naph system has the advantage that the more complex spin system facilitates reliable line shape fitting at the temperature extremes (i.e., well above and below the coalescence temperature), whereas the simple singlet spectra of the phth complexes permit good fitting only in the coalescence region.

Discussion

As noted at the beginning of this paper, previous detailed studies of metal site exchange in naph complexes have been limited to the essentially square-planar species $[AuX(CH_3)_2(dmnaph)]$ and $[cis\text{-}MCl(PR_3)_2(naph)]^+$, M = Pt and Pd.[6,7] These investigations led to the conclusion that the most likely mechanism for dynamic behavior is an intramolecular process for which the transition state involves naph bound to the metal via both nitrogens as a symmetric chelate. In the case of the platinum complexes dissociative mechanisms involving metal–nitrogen bond cleavage can be specifically excluded since $^{195}Pt-^{1}H$ spin–spin coupling is distinguishable at the fast-exchange limit[6] whereas for the more labile palladium complexes there is evidence that both intramolecular and dissociative processes occur.[7] In $[cis\text{-}PtCl(PEt_3)_2(phth)]^+$, $^{195}Pt-^{1}H$ coupling is not maintained at the fast-exchange limit and a dissociative mechanism is indicated.[6] The observed activation energies ($\Delta G^{\circ\ddagger}_{T_c}$) at the coalescence temperatures (T_c) reflect these mechanistic differences with the intramolecular process in naph complexes (~44 kJ mol^{-1} for Au, ~51 kJ mol^{-1} for Pt) being more facile than the dissociative process in phth complexes (~76 kJ mol^{-1}). The $\Delta G^{\circ\ddagger}_{298}$ values shown in Table I for the $[M(CO)_5L]$ complexes, L = naph or phth, are thus closely comparable with the literature data for Au and Pt complexes, suggesting that a similar mechanistic interpretation may be appropriate; however, insufficient data are yet available relating to either intra- or intermolecular exchange involving M–N bonds to comment meaningfully on the fact that the $\Delta G^{\circ\ddagger}_{298}$ values are near-identical for M = Cr or W complexes of each of the ligands under discussion.

The results for phth complexes in Table I may also be compared with those for a series of $[(aryl)Cr(CO)_2$(2,3-diazabicyclo[2.2.1]hept-2-ene] complexes[10] and with those for the Cr and W complexes[11,12] $[M(CO)_5$(benzo[*c*]cinnoline)]. For the first type, activation energies ($\Delta G^{\circ\ddagger}_{T_c}$ = 71.1–82.8 kJ mol^{-1}) are similar to those in Table I for phth complexes, and while an intramolecular process was assumed, the only evidence appears to be the reversibility of the variable-temperature spectra[10] and a dissociative process seems equally likely. In the benzo[*c*]cinnoline case, no thermodynamic parameters were calculated but since a dynamic process is already fast for the Cr complex at ambient temperature[11,12] a lower activation energy is likely: it has been suggested that this is associated with low-lying π^*(N=N) orbitals.[12] There is, however, disagreement over the rate in $[W(CO)_5$(benzo[*c*]cinnoline)], one group reporting it to be fluxional at ambient temperature[12] and the other rigid.[11] The reason for this conflict is not clear, but it seems possible that the complexes are difficult to obtain pure.

Experimental Section

Data relating to the characterization of the complexes are given in the Results section and in the preparative descriptions below. Microanalyses were by Canadian Microanalytical Service Ltd., Vancouver, BC. Melting points were determined in open capillary tubes. Mass spectra were recorded with a Perkin-Elmer/Hitachi RMU 7E unit. IR spectra were recorded from 5000 to 200 cm^{-1} with an accuracy of 3 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Solid samples were examined as Nujol mulls between CsI plates. ^1H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer and at 250 MHz on a Bruker WP 250 Fourier transform spectrometer. NMR solvents were dioxane for the phth complexes and acetone-d_6 for the naph complexes with $SiMe_4$ as internal reference in both cases. Simulated NMR spectra were calculated on an IBM 3031 computer and plotted on a Tektronix 4013 graphics screen for preliminary work or a Calcomp 1039 drum plotter for final data. The programs used were a locally constructed package based on DNMR3[14] for dynamic spectra and UEAITR[15] and NMRPLOT[16] for static spectra, iterative refinement, and plotting.

All manipulations were carried out under an atmosphere of dry nitrogen with use of Schlenk tube techniques. Solvents were dried by appropriate methods and distilled under nitrogen prior to use. $Cr(CO)_6$ (Strem Chemicals Inc.), $Mo(CO)_6$ (Alfa-Ventron Corp.), $W(CO)_6$ (Strem Chemicals Inc.), and phthalazine (Aldrich Chemical Co.) were commercially available and were used as received. 1,8-Naphthyridine was prepared as previously described[17] as were its complexes[8] $[M(CO)_5(naph)]$, M = Cr and W.

$W(CO)_5$(phth). A solution of $W(CO)_6$ (0.184 g, 0.52 mmol) in tetrahydrofuran (100 mL) was irradiated in a Pyrex glass tube for 8 h with a Hanovia 450-W UV lamp. Phthalazine (0.068 g, 0.52 mmol) in tetrahydrofuran (10 mL) was added, and the initially yellow solution changed to red. The mixture was stirred overnight, during which time the color returned to yellow; solvent was removed in vacuo and unreacted $W(CO)_6$ removed by sublimation. The residue was recrystallized from 1:4 THF/hexane at −25 °C to give $W(CO)_5$(phth) as an orange-brown microcrystalline solid (0.17 g, 0.37 mmol), mp 130–140 °C dec. Anal. Calcd for $C_{13}H_6N_2O_5W$: C, 34.39; H, 1.33; N, 6.17. Found: C, 34.30; H, 1.39; N, 5.66.

$Cr(CO)_5$(phth). A similar procedure using $Cr(CO)_6$ (0.30 g, 1.36 mmol) in methanol (30 mL) with phthalazine (0.177 g, 1.36 mmol) yielded $Cr(CO)_5$(phth) as orange-yellow crystals (0.22 g, 0.68 mmol), mp 130–135 °C dec. Anal. Calcd for $C_{13}H_6N_2O_5Cr$: C, 48.46; H, 1.88; N, 8.70. Found: C, 49.28; H, 1.44; N, 8.67.

Acknowledgment. We thank the NSERC, Canada, and the University of Victoria for financial support.

Registry No. $Cr(CO)_5$(phth), 83061-16-9; $W(CO)_5$(phth), 83061-17-0; $Cr(CO)_5$(naph), 41119-94-2; $W(CO)_5$(naph), 41119-95-3.

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(18) The term noncoordinated is used here only to distinguish between the two rings in the naph skeleton and is not intended to exclude the possibility of a weak interaction between the metal and the more distant nitrogen atom.

Contribution from the Inorganic Chemistry
and Crystallography Departments, University of Nijmegen,
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Gold Clusters. Tetrakis[1,3-bis(diphenylphosphino)propane]hexagold Dinitrate: Preparation, X-ray Analysis, and ^{197}Au Mössbauer and $^{31}P\{^1H\}$ NMR Spectra

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Gold cluster compounds are of interest because of their remarkable structures but also because of the rather fast in-

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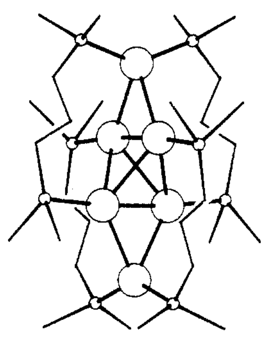

Figure 1. Drawing of the $[Au_6(P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2)_4](NO_3)_2$ cluster.

terconversion reactions. In many of these reactions a partial or complete fragmentation of the original cluster into smaller molecules is followed by a recombination to new clusters. As $[Au_9L_8]^{3+}$ (L = PPh_3) seems to be a key compound in many reactions,[1-5] its fragmentation–recombination reactions have been studied. In reaction with L, $[Au_8L_8]^{2+}$ and $[Au_8L_7]^{2+}$ are formed,[1,2,4] with Cl^-, $[Au_{11}L_8Cl_2]^+$,[3] with SCN^-, $Au_{11}L_7(SCN)_3$,[3] and with I^-, $Au_4L_4I_2$.[5] With bidentate phosphines of the type $Ph_2P(CH_2)_nPPh_2$ the reaction product critically depends on n. With $n = 1$ $[Au_5(Ph_2PCH_2PPh_2)_3(Ph_2PCHPPh_2)]^{2+}$ is formed,[6,7] but with $n = 3$ (dppp) the completely different $[Au_6(dppp)_4]^{2+}$ is formed. We describe here the crystal and molecular structure of $Au_6[P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2]_4(NO_3)_2$. It crystallizes probably in space group $P\bar{4}c2$, but the disordered structure was refined in space group $P\bar{4}m2$ with $a = b = 14.726$ (5) Å, $c = 16.879$ (4) Å, $V = 3660.3$ Å^3, and $Z = 1$. On the basis of 723 unique observed reflections the structure has been refined to $R = 0.094$. Also presented are the conversion reaction of $Au_4L_4I_2$ into $[Au_6(dppp)_4]^{2+}$ and the ^{197}Au Mössbauer and ^{31}P NMR spectra of both compounds with some remarks about the interpretation of these spectra for gold cluster compounds in general.

Experimental Section

Synthetic Work. $[Au_9L_8](NO_3)_3$[8] and $Au_4L_4(\mu\text{-}I)_2$[5] were prepared by literature methods. All other starting materials were commercially available. Chemical analyses were carried out by Dr. A. Bernhardt, Elbach über Engelskirchen, West Germany. The ^{197}Au Mössbauer spectra were recorded at 4.2 K with an apparatus described earlier.[9] The $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-100 FT spectrometer using CD_2Cl_2 as solvent and internal lock and $OP(OMe)_3$ (TMP) as external standard. The ESR spectra were recorded with a Varian E12 spectrometer.

Preparation of $[Au_6[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_4](NO_3)_2$. To a solution of 1 g of $[Au_9L_8](NO_3)_3$ in 25 mL of methylene chloride is added 2 g of $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ (mole ratio 1:20). A fast reaction occurs, as indicated by a change of color from red into a very intense blue within 2 min. After 15 min the product is precipitated by addition of 200 mL of toluene. After filtration and washing with toluene and ether, the blue product is recrystallized by diffusion of a methylene chloride solution into diethyl ether, resulting in thin rectangular plates, with a clear bright red color. When the crystals dry (in vacuo or in air), they crack because of solvent loss, turning into an untransparent purple-red; yield 500 mg (46% based on Au). Anal. Calcd for $C_{108}H_{104}Au_6N_2O_6P_8$, $M_r = 2955.639$: C, 43.89; H, 3.55; N, 0.95. Found: C, 43.20; H, 3.54; N, 0.92. IR (CsI pellet): only bands originating from free nitrate and bonded dppp can be assigned. $^{31}P\{^1H\}$ NMR: two quintets of equal intensity at −51.07 and −60.24 ppm (downfield relative to TMP in CD_2Cl_2), with a coupling of 5.0 ± 0.2 Hz. ^{1}H NMR (CD_2Cl_2, relative to Me_4Si): 7.6–6.6 ppm, multiplet, aromatic protons (80 H); 3.0, broad, aliphatic protons ($C\text{–}CH_2\text{–}C$, 8 H); 2.2, broad ($P\text{–}CH_2$, 16 H). ESR: no signal could be detected in the solid state or in solution (CH_2Cl_2). This is in accordance with the formula of the compound.

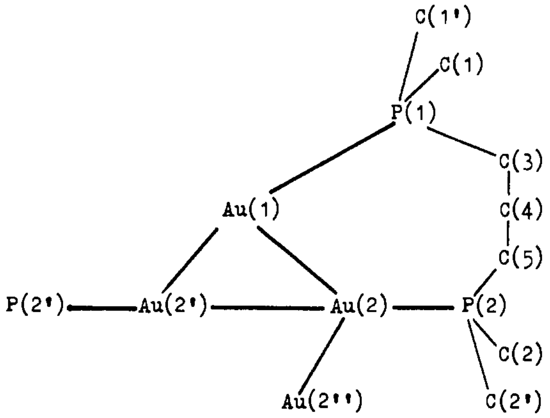

Figure 2. Atom-numbering scheme for the $[Au_6(P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2)_4]^{2+}$ cluster.

Table I. Experimental Details of the X-ray Diffraction Study of Tetrakis[1,3-bis(diphenylphosphino)propane]hexagold Dinitrate

formula	$C_{108}H_{104}Au_6N_2O_6P_8\cdot xCH_2Cl_2$
probable space group	$P\bar{4}c2$
a, Å	14.726 (5)
b, Å	14.726 (5)
c, Å	33.758 (8)
V, Å^3	7320.6
Z	2
refinement space group	$P\bar{4}m2$ (disorder assumed; see text)
a, Å	14.726 (5)
b, Å	14.726 (5)
c, Å	16.879 (4)
V, Å	3660.3 Å^3
Z	1
instrument	Nonius CAD-4 diffractometer
radiation used	Cu Kα, graphite monochromated ($\lambda = 1.5418$ Å)
type of scan	$\omega\text{–}2\theta$
no. of measd reflctns	5532
no. of indep reflctns	723
no. of data with $I > 3\sigma(I)$	318
final R value	0.094

Conversion of $Au_4L_4I_2$ into $[Au_6(PPh_2(CH_2)_3PPh_2)_4]^{2+}$. Exactly the same procedure as above was followed, but instead of 1 g of $[Au_9L_8](NO_3)_3$, 400 mg of $Au_4L_4I_2$ was used.

Crystallographic Work. Thin rectangular red crystals, suitable for an X-ray structure determination, were mounted in a sealed capillary to prevent loss of solvent. X-ray analysis revealed the molecular structure of the $[Au_6(PPh_2(CH_2)_3PPh_2)_4]^{2+}$ cluster (Figure 1).

Crystal data: $Au_6C_{108}H_{104}N_2O_6P_8\cdot xCH_2Cl_2$, tetragonal, Laue symmetry $4/mmm$, probable space group $P\bar{4}c2$ with unit cell $a = b = 14.726$ (5) Å, $c = 33.758$ (8) Å, $V = 7320.6$ Å^3, and $Z = 2$. The disordered structure was refined in space group $P\bar{4}m2$ with unit cell $a = b = 14.726$ (5) Å, $c = 16.879$ (4) Å, $V = 3660.3$ Å^3, and $Z = 1$ (Table I). The X-ray data were measured on a Nonius CAD-4 diffractometer $\omega\text{–}2\theta$ scan, with monochromated Cu Kα radiation. When exposed to X-ray radiation, the crystal decomposed slowly. A total of 5532 reflections were measured; averaging symmetry- and Friedel-dependent reflections gave 723 independent reflections. The l = odd reflections were very weak: only six of these had $I > 3\sigma(I)$

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Table II

(a) Positional Parameters for $[Au_6(dppp)_4](NO_3)_2$

atom	x	y	z	atom	x	y	z
Au(1)	0	0	0.2131 (7)	C(1)	0.187	0.119	0.308
Au(2)	0.0893 (7)	0	−0.0668 (5)	C(2)	0.277	0.100	−0.136
P(1)	0.154 (5)	0	0.259 (5)	C(3)	0.230	0	0.185
P(2)	0.249 (5)	0	−0.055 (5)	C(4)	0.180	0	0.098
				C(5)	0.275	0	0.055

(b) Thermal Parameters (U_{ij} Values × 100)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	atom	U_{11}	U_{22}	U_{33}	U_{23}
Au(1)	11	15	4.4	0	P(2)	15	23	0.2	0
Au(2)	13	12	3.8	0	C(all	25	25	25	0
P(1)	11	34	3.6	0.9	unrefined)				

[a] All U_{12} and U_{13} values are 0 for the atoms given.

Table III. Some Bond Distances (Å) and Angles (Deg) for $[Au_6(dppp)_4](NO_3)_2$

Au(1)-Au(2)	2.80 (1)	Au(1)-P(1)	2.39 (8)
Au(2)-Au(2′)	2.63 (1)	Au(2)-P(2)	2.36 (8)
Au(2)-Au(2″)	2.92 (1)		
Au(2)-Au(1)-Au(2′)	56.1 (4)	P(2)-Au(2)-Au(2′)	175.0 (5)
P(1)-Au(1)-P(1′)	142.1 (9)		

($\sigma(I)$ based on counting statistics). Inspection of the Patterson synthesis showed the presence of two identical Au_6 clusters, separated by $^1/_2c$ translation. In applying the DIRDIF procedure,[10] we found all phosphorus atoms, which obeyed the same $^1/_2c$ translation. Therefore, all gold and phosphorus atoms lie on pseudo mirror planes ($x = 0$ or $y = 0$). We tried to develop a model without this mirror symmetry, but the six l = odd reflections were not numerous enough to permit us to do so. The propylene bridge could roughly be located in the pseudo mirror plane, although it can hardly be imagined that the atoms of the P–C–C–C–P chain lie in one plane. The structure is more relaxed when deviations out of plane are allowed, this being possible without major changes in the overall geometry of the molecule. Because of the failure to locate the phenyl rings, we assume that the structure is disordered, although the disorder cannot be perfect because of the l = odd reflections. Refinement was continued in space group $P\bar{4}m2$ on 318 observed reflections, with the original l = odd reflections discarded. The Au and P atoms were refined with anisotropic temperature parameters, while the carbon atoms were kept fixed. The phenyl carbons, attached to the phosphorus atoms, could very roughly be located, but large areas of positive electron density in the expected positions of the phenyl groups could not be interpreted in terms of atomic positions. In addition, the often disordered nitrate ions and methylene chloride molecule(s) were not located. The refinement was stopped at $R = 0.094$. Positional parameters are given in part a of Table II and thermal parameters in part b; the large U_{22} values for the phosphorus atoms reflect the disorder across the space-group mirror plane. Some bond distances and angles are given in Table III.

Results and Discussion

Both $Au_4L_4I_2$ and $[Au_9L_8]^{3+}$ react with dppp to give $[Au_6(dppp)_4]^{2+}$ in striking difference with $Au_{11}L_7X_3$, which when reacted with dppp yields only the completely substituted product $[Au_{11}(dppp)_5]^{3+}$.[11] The conversion of $Au_4L_4I_2$ into $[Au_6(dppp)_4]^{2+}$ is another example of a reaction whose explanation needs the assumption of small reactive molecules containing phosphine and one, two, or three Au atoms in an average oxidation state between 0 and 1. Except for a preliminary report[12] about Au_2L_2, no such small fragment has been identified until now.

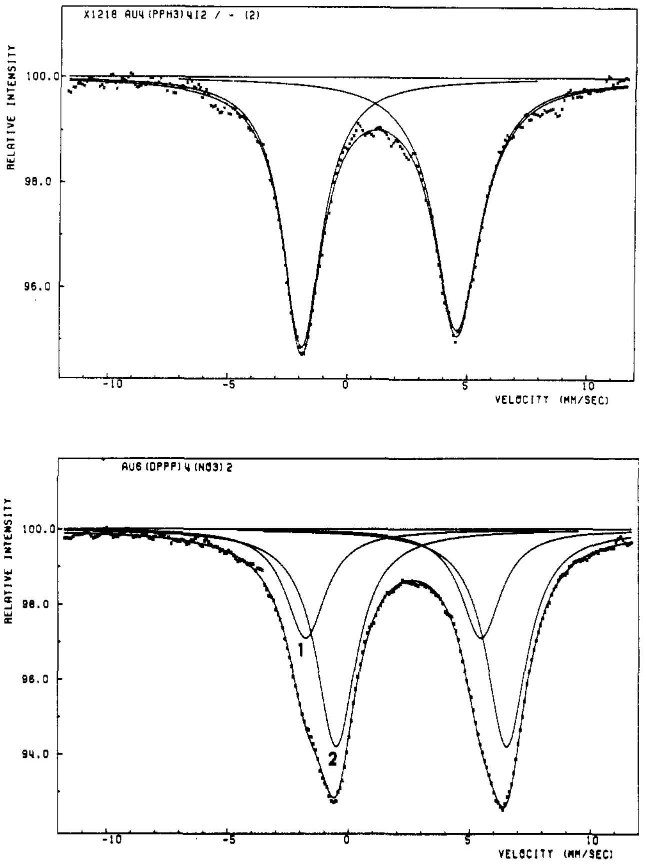

Figure 3. ^{197}Au Mössbauer spectra of $Au_4L_4I_2$ and $[Au_6(P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2)_4](NO_3)_2$, fitted with respectively two lines (line width 1.96, 2.34 mm/s) and four lines (line width 2.05 and 2.10 mm/s).

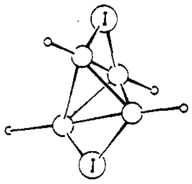

Figure 4. Au–P skeleton of $Au_4L_4I_2$: (◯) Au; (○) P.

Table IV. ^{197}Au Mössbauer Parameters for Some Gold Cluster Compounds[a]

	P-Au–Au-P	Au–bridging atom	Au–L
$[Au_6(dppp)_4](NO_3)_2$	3.0 (7.0)	1.9 (7.2)	
$Au_4L_4I_2$	1.4 (6.5)		
$Au_{11}L_7(CN)_3$			1.5 (6.5)
$Au_9L_8{}^{3+}$			2.1 (6.6)
$Au_8L_8{}^{2+}$			1.9 (6.7)
$Au_{11}(dppp)_5{}^{3+}$			1.7 (6.6)

[a] Isomer shift (relative to ^{197}Pt source) and quadruple splitting values (in parentheses) are given in mm/s.

The Mössbauer spectra of $Au_4L_4I_2$ and $[Au_6(dppp)_4]^{2+}$ are illustrated in Figure 3. The spectrum of $[Au_6(dppp)_4]^{2+}$ can be successfully fitted by assuming two gold sites each giving a quadrupole pair, the pairs having an intensity ratio of 1:2 and line widths close to the natural line width. The spectrum is thus in accord with the structure of $[Au_6(dppp)_4]^{2+}$ (see Figure 1). A set of four equivalent Au atoms is situated on the vertices of a tetrahedron and bonded to one phosphino group. A set of two Au atoms bridges opposite edges of the tetrahedron and is bonded to two phosphino groups. This structure resembles that of $Au_4L_4I_2$, where also a tetrahedron

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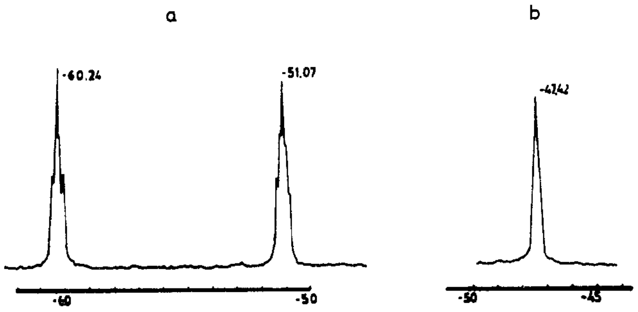

Figure 5. $^{31}P\{^1H\}$ NMR spectra of (a) $[Au_6(P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2)_4](NO_3)_2$ and (b) $Au_4L_4I_2$.

of four Au atoms is present and I atoms bridge over two opposite edges[5] (see Figure 4). In both clusters there are almost linear P–Au–Au–P moieties with very short Au–Au bond lengths (2.65 and 2.63 Å) as compared to the other Au–Au distances (2.80–2.92 Å). In accord with its structure the Mössbauer spectrum of $Au_4L_4I_2$ shows only one quadrupole pair. The Mössbauer parameters are given in Table IV compared with data of P-connected Au sites in some Au cluster compounds. Quadrupole splittings and isomer shifts are in rather narrow ranges. Neither the presence or absence of a central gold nor the connection to one or two phosphines gives clearly distinct data. So the conclusion that we formulated earlier[13,14] about the ratio of radial to tangential interactions seems to be in doubt with regard to the present data.

The $^{31}P\{^1H\}$ NMR spectrum of $[Au_6(dppp)_4]^{2+}$ in CD_2Cl_2 solution shows two sets of quintets of equal intensity, positioned at −51.07 and −60.24 ppm (downfield relative to TMP) with a coupling of 5.0 ± 0.2 Hz (see Figure 5). The spectrum is in agreement with the presence of two magnetically inequivalent sets of four P atoms, coupled via the Au skeleton. No additional coupling via the propylene bridge could be detected. The $^{31}P\{^1H\}$ NMR spectrum of $[Au_4L_4I_2$ shows one singlet at −47.4 ppm (see Figure 4).

Except for the spectrum of $[Au_5(Ph_2PCH_2PPh_2)_3(Ph_2PCHPPh_2)]^{2+}$, which is rather complex,[6,7] the spectra of all other gold clusters containing monodentate phosphine and even $[Au_{11}(dppp)_5]^{3+}$ show one singlet.[11] The solid-state spectrum of $[Au_9L_8](NO_3)_3$ has two lines of about equal intensities[15] in accordance with the two crystallographically distinct sets of four P atoms. No P–P coupling could, however, be detected. The presence of one singlet in the solution spectra finds its best explanation in a fast intramolecular equilibration of the P sites, a process that is less probable for the more rigid $[Au_5(Ph_2PCH_2PPh_2)_3(Ph_2PCHPPh_2)]^{2+}$ and $[Au_6(dppp)_4]^{2+}$ clusters.

Acknowledgment. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO).

Registry No. $[Au_6[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_4](NO_3)_2 \cdot xCH_2Cl_2$, 83060-80-4; $[Au_9L_8](NO_3)_3$, 37336-35-9; $Au_4L_4I_2$, 78519-63-8; Au, 7440-57-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Dinuclear Copper(I) Benzoato Complexes Containing Acetylenes: Synthesis, Structure, and Reactivity with Molecular Hydrogen

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Cuprous carboxylato species are considered the first well-documented examples of complexes involved in homogeneous catalyzed hydrogenation.[2a] In spite of this, the reactivity of copper(I) carboxylato derivatives with unsaturated substrates which potentially can undergo hydrogenation is very poorly explored. We can mention that copper(I) promotes the activation of the H_2 molecule by heterolytic splitting,[2b] which would be highly interesting for the hydrogenation of molecules containing oxygen atoms, like CO and CO_2. A further interest in copper(I) carboxylato derivatives comes from the fact that a bimetallic unit seems to survive in their reactions with various σ ligands.[3] This observation was further confirmed by the result obtained in the reaction of copper(I) acetate with olefins, although no structural evidence supports this hypothesis.[4] Very recently, however, it was found that the reaction of copper(I) benzoate with carbon monoxide led, in the presence of ancillary ligands, to the isolation of the first dicopper(I) unit containing a bridging carbonyl.[5]

The present report concerns the reactivity of copper(I) benzoate with disubstituted acetylenes leading to the isolation and structural identification of dinuclear copper(I) acetylene complexes. The fact that copper(I) has a rich chemistry with acetylenes notwithstanding,[6-8] we are dealing with the first model complexes having a disubstituted acetylene coordinated to a low-nuclearity copper(I) system.

Experimental Section

Owing to the air sensitivity of the complexes, all operations were carried out in a dry oxygen-free nitrogen atmosphere, with use of standard Schlenk techniques. Solvents were purified and dried by standard methods. Acetylenes were recrystallized or distilled before use. A modified procedure was used for the preparation of $[Cu(PhCO_2)]_4$.[5,9] IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

Reaction of Diphenylacetylene with Copper(I) Benzoate. Copper(I) benzoate (0.53 g, 0.72 mmol) was added to a methanolic solution (20 mL) of Ph_2C_2 (0.52 g, 2.92 mmol). A microcrystalline white solid immediately formed (0.70 g, 66.1%), while the mother solution cooled at 0 °C gave crystals suitable for the X-ray analysis. Both precipitates were shown to be the same compound. Anal. Calcd for $[Cu(PhCO_2)(Ph_2C_2)]_2$, $C_{42}H_{30}O_4Cu_2$: C, 69.52; H, 4.14. Found: C,

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