$CpW(CO)_3(C_5H_{11})$.[30] Direct evidence for the intermediacy of $CpW(CO)_2CH_3$ in the formation of $Cp_2W_2(CO)_6$ comes from the warm-up experiments on $CpW(CO)_2(THF)CH_3$. A solution of this complex in THF at −78 °C is stable, but upon warming the solution to room temperature, the complex disappears and $Cp_2W_2(CO)_6$ forms (as well as some $CpW(CO)_3CH_3$). The obvious interpretation of these observations is that upon warming, the weak W–THF bond is broken thereby generating $CpW(CO)_2CH_2$ which reacts to form the coupled product. (All of the reactants which might be necessary for further reaction of $CpW(CO)_2CH_3$ are still in the cell; unreacted $CpW(CO)_3CH_3$ is present as well as the CO generated during the photolysis. The sealed cell is gastight.)

The question remains: what two species are coupled to form the binuclear product? Because the disappearance quantum yield for reaction 10 is independent of the light intensity, the binuclear product is probably not formed by the coupling of two photochemically generated intermediates.[31] For this reason, the pathway in eq 5–8 is not suggested. The observation that $Cp_2W_2(CO)_6$ forms before $CpW(CO)_3Cl$ in chlorocarbon solvents is also not consistent with this mechanism. A likely pathway for the coupling involves the reaction of $CpW(CO)_2CH_3$ with an unreacted molecule of $CpW(CO)_3CH_3$ (eq 13). Addition of CO to $Cp_2W_2(CO)_5$ would give the product (eq 14). This mechanism is consistent with the intensity-independent quantum yield and with the observation that $CpW(CO)_3$ is not formed. We propose that one of the sources of the extra hydrogen atom for the CH_3 radical to form CH_4 is the solvent. Mass spectral analyses showed that substantial amounts of CH_3D are formed during the photolysis of $CpW(CO)_3CH_3$ in benzene-d_6 and chloroform-d solvents. Control experiments using NMR showed that the hydrogen atoms on the cyclopentadienyl rings do not exchange with the deuterium atoms in the deuterated solvents on the time scale of the photochemical experiments. Hence, the cyclopentadienyl ring is not a major source of the deuterium in CH_3D.

$$CpW(CO)_2CH_3 + CpW(CO)_3CH_3 \rightarrow Cp_2W_2(CO)_5 + 2CH_3 \quad (13)$$

$$Cp_2W_2(CO)_5 + CO \rightarrow Cp_2W_2(CO)_6 \quad (14)$$

The reaction of a coordinatively unsaturated 16-electron complex with a coordinatively saturated molecule as proposed in eq 13 is not uncommon for metal carbonyl complexes. The photochemical reaction of $Fe(CO)_5$ to form $Fe_2(CO)_9$ occurs by reaction of $Fe(CO)_4$ with an $Fe(CO)_5$ molecule.[32] A similar mechanism was shown for the photochemical formation of $Cp_2Co_2(CO)_3$ from $CpCo(CO)_2$.[33] In addition, Norton has proposed binuclear elimination mechanisms for the thermal decompositions of $H_2Os(CO)_4$[12b] and $HOs(CO)_4CH_3$.[12c] For both complexes, a key step in the decomposition is the reaction of a coordinatively unsaturated complex with a coordinatively saturated one.

Registry No. $CpW(CO)_3CH_3$, 12082-27-8; $Cp_2W_2(CO)_6$, 12091-65-5; $CpW(CO)_3Cl$, 12128-24-4; $CpW(CO)_2(PPh_3)(COCH_3)$, 53079-50-8; $CpW(CO)_2Cl_3$, 12107-08-3; $CpW(CO)_2(AsPh_3)CH_3$, 77462-49-8; $CpW(CO)_2(CH_3CN)CH_3$, 77462-48-7; $CpW(CO)_2(THF)CH_3$, 77462-47-6; $CpW(CO)_2(PPh_3)CH_3$, 12115-41-2.

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Binuclear Copper(I) Complexes Which Reversibly React with CO. 1. Di-μ-halogeno-bis(2,2′-bipyridine)dicopper(I) and Its Derivatives

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Binuclear copper(I) complexes $[CuXL]_2$ and mononuclear copper(I) complexes $[CuL_2]X$ (X = Cl, Br, and I; L = 2,2′-bipyridine and 1,10-phenanthroline) have been synthesized in acetone and ethanol, respectively. The complexes $[CuXL]_2$ react with CO reversibly to give crystalline carbonyl adducts, which are stable at low temperature. The isolated crystalline product exhibits $\nu_{CO} = 2066\ cm^{-1}$, which is consistent with the carbonyl species in acetone solution. The carbonyl adducts are found to be five-coordinate complexes having bridged halogen atoms with the stoichiometry of 1 CO/2 Cu. The affinity of $[CuXL]_2$ for CO is influenced by the bridged halogen and solvent used. The formation constants of the carbonyl adducts increase in the order Cl < Br < I, and solvents with lower dielectric constants favor the formation of the adducts. The mononuclear complexes $[CuL_2]X$ show no affinity for CO. The flexibility of the binuclear complex, associated with the bridged halogen atoms, is a significant factor governing the reactivity toward CO.

Introduction

Carbonyl complexes of copper are confined to the copper(I) oxidation state. Recent activity in this area has been motivated by a desire to elucidate the relationship between structure and reactivity toward carbon monoxide with respect to Cu(I) complexes. Hemocyanin,[1] a copper-containing respiratory protein, also binds CO reversibly.[2] Studies on the carbonyl complex may help to explore the ligand environment in the hemocyanin active site. There are a few stable (i.e., isolable under ambient condition) copper(I) carbonyl complexes in a variety of carbonyl complexes. However, the characterization has not yet been ascertained. Recent synthetic challenges provide us with some thermally stable carbonyl complexes which are characterized by X-ray structural analysis,[3-5,8] in-

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frared spectra,[4,5,7,8] and other physicochemical measurements.[8-10] In general, copper(I) complexes have been found to bind CO if a fourth coordination site is available.[3-6] On the other hand, several square-planar four-coordinate complexes bind CO as a fifth ligand,[7-10] as illustrated by Cu(DOBF$_2$).[7,11] However, the factors which control CO-binding ability of Cu(I) complexes are not necessarily settled because the five-coordinate carbonyls are still an exceptional case.

Polydentate macrocyclic ligands have been preferably employed to provide a well-defined ligand environment in solution. In the copper(I) complex, the macrocyclic ligand may tightly bind Cu(I) atom at a sacrifice of the flexibility of geometry around the Cu(I) atom. Such a lack of flexibility of the structure may reduce affinity for CO, especially, in the tetrahedral four-coordinate complex, because the steric barrier to the conformational change of the complex is larger than that of four-coordinate square-planar or three-coordinate complex.[12] The extensive study is also restricted to the sophisticatedly synthesized macrocyclic ligand which provides a novel carbonyl adduct by getting over the handicap to the rigid structure.

In comparison with multidentate macrocyclic ligands, the mono- and bidentate ligands which are usually available, afford characteristic ligand environments: desirable combination of ligands and flexibility of geometry in the resultant copper(I) complex are potentially advantageous. Despite such a potent utility, there have been few studies on stability, structure, and reactivity of the mixed-ligand copper(I) complex while a vast body of data on the Cu(II) complexes have been accumulated. This is because Cu(I) complexes are diamagnetic, and hence, provide no optical absorption bands[13] and no electron spin resonance signals. This makes it difficult to characterize structure, and properties of Cu(I) complexes, especially in solution. We are, however, endeavoring to catalog fundamental copper(I) coordination chemistry in solution.[12] Keen interest in Copper(I) with high affinity for CO and/or O$_2$ prompts us to synthesize mononuclear or binuclear Cu(I) complexes. The purpose of this work is to present simple copper(I) complexes without macrocyclic ligand systems, which reversibly react with CO in both solution and solid state.

Experimental Section

Materials. The reagent grade copper(I) chloride was purified according to the literature.[14] Both copper(I) bromide and iodide were used without further purification. They were all dried in vacuo (75–100 °C). [Cu(CH$_3$CN)$_4$]ClO$_4$ was prepared in the usual way[15] and recrystallized from ether under nitrogen atmosphere. The reagent grade AgClO$_4$ was utilized without further purification. 2,2′-Bipyridine (bpy), 2,2′-bis(4-methylpyridine) (bpc), and 1,10-phenanthroline (phen) were commercially available. They were recrystallized several times from acetone and dried in vacuo before use.

Acetone treated with potassium permanganate was dried over potassium carbonate, distilled, and then fractionally distilled from 4-Å molecular sieves. 2-Butanone and 4-methyl-2-pentanone (MP) were also purified in the similar way. Ethanol and *tert*-butyl alcohol (*t*-BuOH) were dried[16] and distilled before use.

Sample preparation of the air-sensitive materials was accomplished under a nitrogen atmosphere. Nitrogen gas with a high purity (99.9995%) was used.

[Cu^{I}Cl(bpy)]$_2$. CuCl is insoluble in acetone while the resultant bpy complex is moderately soluble in acetone (<10 mM). In the presence of an equal amount of bpy (0.5 mM), CuCl was completely soluble in acetone for 4 h, exhibiting the complete formation of the bpy complex.

A solution of bpy (156 mg, 1.0 mM) and anhydrous CuCl (98 mg, 1.0 mM) in 50 mL of acetone was stirred under nitrogen at 25 °C for 4 h. The brown microcrystalline product precipitated gradually. It was filtered off, washed twice with deaerated acetone, and evaporated under a stream of nitrogen. Anal. Calcd for $C_{20}H_{16}N_4Cl_2Cu_2$: C, 47.06; H, 3.14; N, 10.98. Found: C, 47.1; H, 3.6; N, 11.0.

The bromo and iodo complexes were also prepared by the similar way.

Cu$^I_2$Cl$_2$(bpy)$_2$CO. A solution of bpy (156 mg, 1.0 mmol) and CuCl (98 mg, 1.0 mmol) in 50 mL of acetone was stirred under nitrogen for 4 h. Carbon monoxide was then added to the deposited solution, the initially brown solution becoming pale yellow and the precipitate dissolving into acetone. When the solution was cooled at ca. −70 °C, a pale yellow crystal was obtained, which was a stable at low temperature. The crystal slowly released CO to become a brown solid at room temperature. Quick preparation of KBr disk pellets provided IR spectra for Cu$_2$Cl$_2$(bpy)$_2$CO. The carbonyl complex in KBr disk was very stable for many hours. IR data: 2066 cm^{-1} (ν_{CO}).

Physical Measurements. Visible spectra were recorded on a Hitachi 124 spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Solution samples were measured as 10–20 mM acetone solution in 0.05-mm potassium chloride cavity cells by using a polystyrene films as a calibration standard. Proton NMR spectra were measured on a JEOL PS-100 NMR spectrometer using (CH$_3$)$_4$Si as an internal standard. Between 192 and 256 transients were accumulated with use of a 25-μs pulse (90°): 4 K data points were collected over bandwidth of 1250 Hz. All the temperatures were set at −90 ± 2 °C. The solvent utilized was acetone-d_6 (99.8%).

Solution CO Equilibria. The stock solution of [CuCl(bpy)]$_2$ was prepared in advance, and the complete complex formation was checked by monitoring the band at 440 nm. The cell used for determination of solution CO equilibria consisted of a 10-mm quartz cuvette with gas inlet and outlet tubes, by means of which N$_2$ gas containing varying partial pressures of CO can be bubbled through the Cu(I) complex solution. For low-temperature work (below 10 °C), the cavity was flushed with dry nitrogen to prevent condensation. The partial pressure of CO in the gas bubbled through the cuvette was adjusted by mixing pure N$_2$ with pure CO,[17] using two Kusano KG-1 rotameters and two precision needle valves. The rotameters were individually calibrated throughout their ranges with both N$_2$ and CO. By use of this apparatus, partial pressure of CO could be continuously varied from 1.00 to 0.06 atm. Each gas mixture was passed through the cuvette until equilibrium had been attained, as indicated by constancy of absorbance (generally 10–20 min). The concentration of [CuXL]$_2$ (L = bpy and phen; X = Cl, Br, and I) in all cases was 5 × 10^{-4} M.

The fact that the extinction coefficients for the carbonylated and decarbonylated complexes differ permits the equilibrium constant for carbon monoxide to be determined spectrophotometrically. This equilibrium is given by eq 1, where M is the Cu(I) complex studied

$$\mathrm{M} + n\mathrm{CO} \overset{K_{CO}}{\rightleftharpoons} \mathrm{M(CO)}_n \qquad (1)$$

here. The equilibrium constant for this system can be written as eq 2, where C_M is the initial molar concentration of M, C_c the equilibrium

$$K_{CO} = \frac{[\mathrm{M(CO)}_n]}{[\mathrm{M}][\mathrm{CO}]^n} = \frac{C_c}{(C_M - C_c)(P_{CO})^n} \qquad (2)$$

molar concentration of complex, and P_{CO} the equilibrium partial pressure of CO above the solution. According to the usual procedure,[18]

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Table I. Absorption Maxima and Extinction Coefficients for Copper(I) Complexes[a]

complex[b]	solvent	λ_{max}, nm	ϵ_{max},[c] M^{-1} cm^{-1}
$[CuCl(bpy)]_2$	acetone	440	2400[d]
$[CuBr(bpy)]_2$	acetone	440	2400
$[CuI(bpy)]_2$	acetone	436	1600
$[CuCl(phen)]_2$	acetone	440	3800
$[Cu(bpy)_2]Cl$	ethanol	440	4800
$[Cu(phen)_2]Cl$	ethanol	440	6100
$[Cu(bpy)_2]ClO_4$[e]	acetone	440	4800
$[Cu(phen)_2]ClO_4$[e]	acetone	440	6600
$[Cu(bpy)_2]ClO_4$[e]	ethanol	440	5400
$[Cu(phen)_2]ClO_4$[e]	ethanol	440	7000

[a] Formed at 25 °C. $[Cu^+]_0 = 5.0 \times 10^{-4}$ M (total concentration of copper(I) ion. [b] $[L]_0/[Cu^+]_0 = 2.0$ ($[L]_0$ is the total concentration of ligand). [c] Defined as follows: ϵ_{max} = absorbance/$[Cu^+]_0$ (error limit ±50 M^{-1} cm^{-1}). [d] The value of 2400 M^{-1} cm^{-1} was also obtained even in the presence of a large excess of bpy ($[bpy]_0/[Cu^+]_0 = 50$). [e] $[Cu(CH_3CN)_4]ClO_4$ was used as a starting material.

plots of $\log [(A - A_0)/(A_c - A)]$ (=log R) vs. $\log P_{CO}$ can be constructed, where A is the absorbance at wavelength of interest, A_0 is the absorbance of M in the absence of CO, and A_c is the absorbance of the carbonyl complex $M(CO)_n$. The slope of the linear plot affords the coordination number, n, in eq 1 (eq 3). The straight lines were

$$\log R = n(\log P_{CO}) + \log K \tag{3}$$

derived according to eq 3 by use of the method of least squares.[19] Equilibrium constants were determined from the intercepts.

Results and Discussion

A. Formation of Binuclear $[CuXL]_2$ Complexes. Mononuclear Cu(I) Complexes. In the spectra of copper(I) and iron(II) complexes with bpy, there are broad intense bands[20] in the visible region which can be readily distinguished from the ligand bands around 270 nm. The bands in the visible region are not present in other similar cation complexes with bpy, e.g., of nickel and zinc ions. The absorption has been assigned to allowed transitions in which the electron is excited from orbitals primarily localized on the metal to π-antibonding orbitals primarily localized on the ligands ($d\pi \rightarrow \pi^*$).[2,20,21]

$[Cu(bpy)_2]^+$ is readily formed in ethanol or acetone when a solution of $[Cu(CH_3CN)_4]ClO_4$ is added to that of bpy. The method of continuous variations was used to determine the stoichiometry of the complex formed between copper(I) and bpy (or phen) in ethanol or acetone. These data correspond to a bpy (or phen):Cu^I ratio of 2:1 and the stoichiometry of the complex as $[Cu(bpy)_2]^+$ (or $[Cu(phen)_2]^+$). The visible spectra of $[Cu(bpy)_2]ClO_4$ in such solvent show an absorption band at 440 nm with molar extinction coefficient (ϵ_{max}) of ca. 5000 M^{-1} cm^{-1}, while the band for $[Cu(phen)_2]ClO_4$ appears at 440 nm ($\epsilon_{max} \approx 7000$ M^{-1} cm^{-1}) (Table I). The position of the peak maxima is less sensitive to the coordinated ligand such as bpy and phen[20] than the molar extinction coefficient.

Binuclear $[CuXL]_2$ Complexes. When CuCl is used as a starting material, the most remarkable difference in ϵ_{max} values[22] was found between acetone and ethanol solution. In acetone the value of ϵ_{max} (2400 M^{-1} cm^{-1}) is specifically smaller than that in ethanol (4800 M^{-1} cm^{-1}). The principal species in ethanol may be $[Cu(bpy)_2]Cl$ since the ϵ value is almost the same as that of $[Cu(bpy)_2]ClO_4$ in acetone. Large excess of bpy ($[bpy]_0/[CuCl]_0 = 50$) does not influence the absorbance in question, indicating that the value of 2400 M^{-1} cm^{-1} is not simply due to the small population of $[Cu(bpy)_2]Cl$. Hence, anomaly in the ϵ value is attributed to the large population of another solution species with a smaller extinction coefficient than that of $[Cu(bpy)_2]Cl$. On the other hand, such a drastic solvent dependence of the spectra is not encountered for copper(I) complexes from $[Cu(CH_3CN)_4]ClO_4$ (Table I). This implies that a chloride ion is significantly associated with the complex formation. Most probable species is a bridged dimer,[23,24] $[CuCl(bpy)]_2$ (Figure 1), whose type has been known in the copper(I) complex, for example, of [(dimethylamino)phenyl]dimethylarsine.[25] The reaction proceeds according to eq 4. The corresponding isolated products from

$$2CuCl + 2bpy \rightarrow [CuCl(bpy)]_2 \tag{4}$$

acetone were identified as the expected dimer (Cu:bpy:Cl =

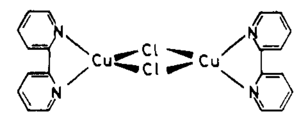
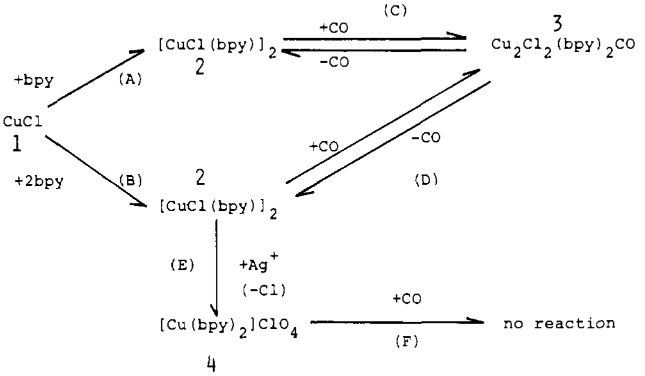


Figure 1. Structure of a binuclear $[CuCl(bpy)]_2$.

Scheme I



Scheme II

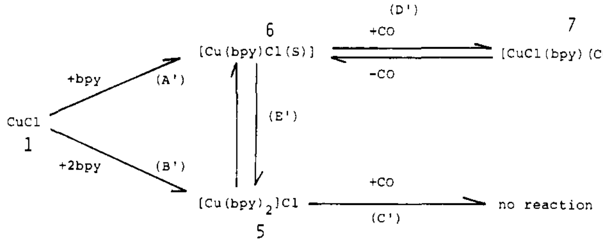


Table II. Effects of Silver Ion on Extinction Coefficients for Copper(I) Complexes

complex[a]	solvent	ϵ,[b] M^{-1} cm^{-1}	ϵ',[c] M^{-1} cm^{-1}
$[CuCl(bpy)]_2$	acetone	2400	4200
$[CuI(bpy)]_2$	acetone	1600	3800
$[CuCl(bpy)]_2$	*t*-BuOH	1150	3300

[a] $[CuX]_0 = 2.5 \times 10^{-4}$ M and $[bpy]_0 = 5.0 \times 10^{-4}$ M at 25 °C. [b] The dominant species is the binuclear complex $[CuX(bpy)]_2$. [c] Addition of 2.5×10^{-4} M $AgClO_4$ to a solution of $[CuX(bpy)]_2$. The resultant complex is mononuclear $[Cu(bpy)_2]ClO_4$.

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(19) Equation 3 contains three unknowns, namely, K, n, and A_c. An approximate value of A_c was obtained from measurements of the solution absorbance at low temperature, where the carbonyl complex is completely formed. The value was between 0.05–0.03. Then A_c was determined by an iterative calculation.

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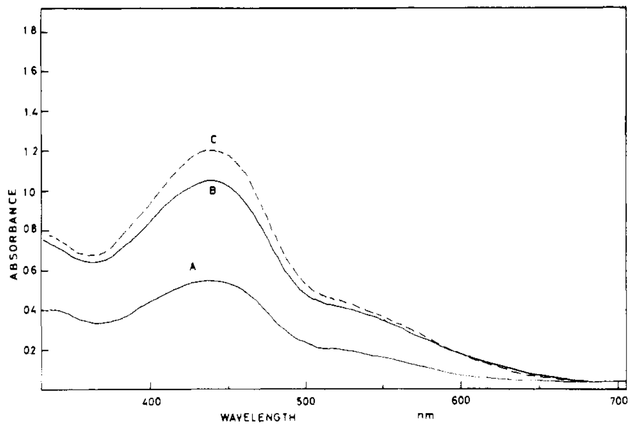

Figure 2. Visible spectra of copper(I) complexes in acetone at 25 °C: (A) 1.3×10^{-4} M of $[CuCl(bpy)]_2$; (B) addition of 2.5×10^{-4} M $AgClO_4$ to a solution of $[CuCl(bpy)]_2$; (C) 2.5×10^{-4} M of $[Cu(bpy)_2]ClO_4$.

1:1:1) by elemental analysis, which is a contrast to the monomer (Cu:bpy:Cl = 1:2:1) from ethanol. The presence of the dimeric compound is also suggested by the poor solubility in acetone (<10 mM). In order to demonstrate the presence of the dimer, we used a comparable amount of $AgClO_4$, which would break down the bridged dimer by rupture of halogen bridging and promotes the complex formation of $[Cu(bpy)_2]ClO_4$ when an excess of bpy is present. The white precipitate of AgCl appeared rapidly upon addition of $AgClO_4$ (eq 5). Figure 2C illustrates that the visible spectrum en-

$$[CuCl(bpy)]_2 + 2AgClO_4 + 2bpy \rightarrow 2[Cu(bpy)_2]ClO_4 + 2AgCl \quad (5)$$

countered an increase in absorbance about twice that of the initial absorbance. The increase in the value of ϵ_{max} is listed in Table II. Scheme I exhibits detailed procedures about the formation of the binuclear copper(I) complexes *in acetone*, while Scheme II shows that the mononuclear copper(I) complexes *in ethanol*. The similar phenomena are also observed in the cases of bromo and iodo derivatives.

The structure of the copper(I) complexes in solution is attributed to solvent used: the halogen-bridged dimer is the dominant form in acetone (Scheme I, procedures A and B), while the monomer is the principal form in ethanol (Scheme II, procedures A′ and B′). Ethanol may suppress the formation of the bridged dimer by rupture of halogen bridging followed by coordination of ethanol molecules to form the [Cu(bpy)Cl(EtOH)]. It is noteworthy in Table II that $AgClO_4$ also affects the absorbance of the band at 440 nm for the Cu(I) complex in *t*-BuOH. This is presumably due to the formation of dimeric complex in *t*-BuOH. The step of Cu–Cl bond fission is likely significant in the complex formation. In polar media such bond fission readily occurs and bis bpy complexes are preferentially formed. *t*-BuOH has lower polarity than ethanol, as has been characterized by a bulk dielectric constant (ϵ), i.e., ϵ(*t*-BuOH) = 12.5 and $\epsilon(C_2H_5OH)$ = 24.6.[26] The trend on the extinction coefficient is, thus, accounted for by the solvent polarity such as the bulk dielectric constant. In conclusion, the formation of the halogen-bridged dimer depends on the coordination ability and/or bulk properties of solvent.

Inspection of Table I reveals that both absorption maxima (λ_{max}) and the extinction coefficient (ϵ_{max}) correlate with the bridged halogen atoms in the order $\lambda_{max}(Cl) \approx \lambda_{max}(Br) > \lambda_{max}(I)$ and $\epsilon_{max}(Cl) \approx \epsilon_{max}(Br) > \epsilon_{max}(I)$. The reflectance spectra of $[CuX(tmb)]_2$ (tmb = 4,6,4′,6′-tetramethyl-2,2′-bipyridine)[23] in the solid state also encounter the similar halogen effect. This implies that the charge-transfer interaction between copper(I) and bpy is subtly controlled by the bridged halogen atom. In the Cu(I) complexes $[CuXL]_2$, π acids other than halide ions can bind the copper(I) atom, competing with bpy, and concurrently weaken the charge-transfer interaction between Cu(I) and bpy. This is well exemplified by decrease of the ϵ_{max} value when carbon monoxide, phosphines, and isocyanides, regarded as good π acids,[27] were added to the $[CuCl(bpy)]_2$ solution.[28] On this viewpoint, the change on the value of ϵ_{max} between halogeno derivatives is also ascribed to the π-back-bonding interaction of the halide ion with the Cu(I) atom: iodine favoring the covalent bonding is a good π-acid rather than chlorine and bromine. Consequently, the charge-transfer band at ~440 nm reflects well the interaction of the Cu(I) atom with bpy and the halide ion. Especially, the extinction coefficient is a sensitive probe to obtain the information about geometric and electronic structures of the present Cu(I) complexes.

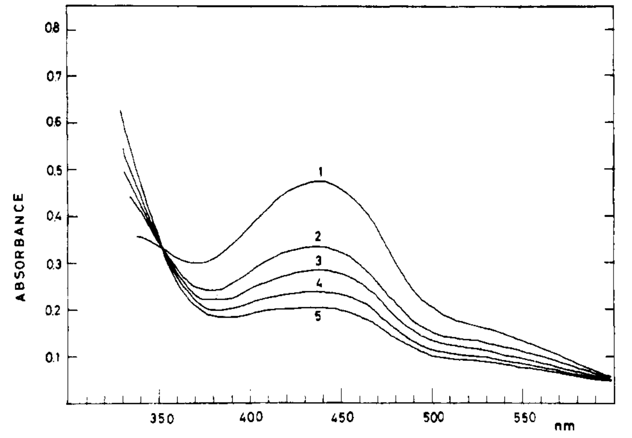

Figure 3. Temperature dependence of spectra of a solution containing 1.5×10^{-4} M of $[CuCl(bpy)]_2$ at 35 °C (1) under an N_2 atmosphere and at 35 (2), 25 (3), 15 (4), and 5 °C (5) under a CO atmosphere.

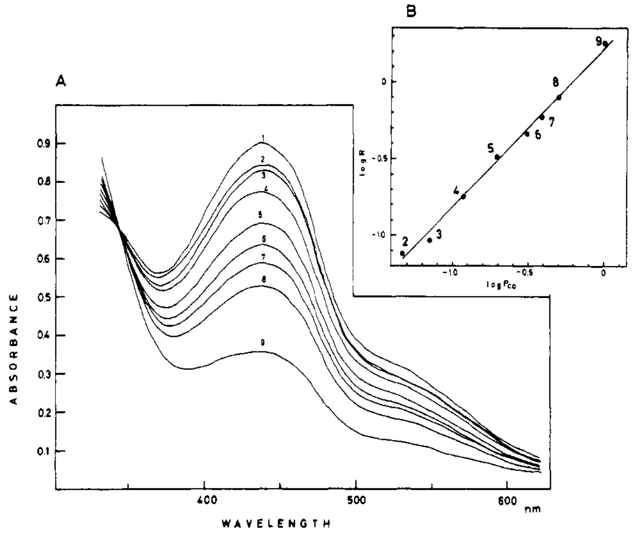

Figure 4. (A) $[CuCl(bpy)]_2$ + CO in 3-butanone at 25 °C. (B) Method of analysis of absorbance data for the reaction of CO with $[CuCl(bpy)]_2$ in 3-butanone.

B. Reversible Reaction of $[CuX(bpy)]_2$ Complex with CO. The brown solution of $[CuX(bpy)]_2$ at 25 °C reacts rapidly

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[26] Riddick, J. A.; Bunger, W. B. "Technique of Chemistry II"; Wiley-Interscience: New York, 1970.

[27] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 2nd ed.; Wiley: New York, 1972; Chapter 27.

[28] Kitagawa, S.; Munakata, M.; Hiroi, Y., manuscript in preparation.

Table III. Equilibrium Constants[a] of Various Copper(I) Complexes

complex	solvent	dielectric const	K_{CO}, atm^{-1}	n[a]
$[CuCl(bpy)]_2$[b]	acetone	20.7	1.3 ± 0.1	1.1 ± 0.1
$[CuCl(bpy)]_2$[c]	acetone	20.7	1.2 ± 0.1	0.99 ± 0.1
$[CuBr(bpy)]_2$	acetone	20.7	3.5 ± 0.3	0.97 ± 0.2
$[CuI(bpy)]_2$	acetone	20.7	6.4 ± 0.3	1.0 ± 0.2
$[CuCl(bpy)]_2$	2-butanone	18.7	1.7 ± 0.1	1.0 ± 0.1
$[CuCl(bpy)]_2$	MP[e]	13.1	3.8 ± 0.1	1.2 ± 0.2
$[Cu(bpy)Cl(S)]$[d]	ethanol	24.6	4.1 ± 0.3	0.8 ± 0.2
$[CuCl(phen)]_2$	acetone	20.7	1.2 ± 0.2	0.9 ± 0.2

[a] For the reactions (i) $[Cu^IXL]_2 + nCO \overset{K_{CO}}{\rightleftharpoons} Cu^I{}_2X_2L_2(CO)_n$ and (ii) $[Cu^IL] + nCO \overset{K_{CO}}{\rightleftharpoons} Cu^IL(CO)_n$ at 25 °C. [b] $[bpy]_0/[CuCl]_0 = 1$. [c] $[bpy]_0/[CuCl]_0 = 2$. [d] $[bpy]_0/[CuCl]_0 = 1$. S = solvent. [e] MP = 4-methyl-2-pentanone.

Table IV. ^1H NMR Chemical Shifts[a] for Copper(I) Complexes in Acetone[b]

complex	6-H	3-H	4-H	5-H
bpy	8.66	8.45	7.94	7.45
$[CuCl(bpy)]_2$	(8.58)[c]	(8.56)[c]	8.08[d]	7.57
$Cu_2Cl_2(bpy)_2CO$	(8.98)[e]		8.22[d]	(7.76)[e]

[a] Shift in ppm from $(CH_3)_4Si$. [b] −90 ± 2 °C. [c] Accidentally collapsing each other to become an unresolved broad band. [d] Assigned from bpc derivatives. [e] Unresolved broad bands which are not assigned.

with CO to give pale yellow solutions. Purging the yellow solution with N_2 rapidly restores the brown color. This process can be repeated many times without apparent decomposition. This complex shows the high degree of reversivility as well as several carbonyl adducts reported by Gagnē.[7,10] Figures 3 and 4 depict the series of spectra of the CO treated solution of $[CuCl(bpy)]_2$ (**2**) upon varying temperature under constant CO pressure (Figure 3) and partial CO pressure (Figure 4), respectively. In Figure 3, an isosbestic point at 352 nm is indicative of the equilibrium expressed by eq 1. Cooling the solution drives the equilibrium to the carbonyl adduct; especially cooling to −70 °C yields a pale yellow solution, indicating the complete formation of the carbonyl adduct which shows no absorption band in the visible region. Rewarming the pale yellow solution to 25 °C restores the brown color. On the other hand, $[Cu(bpy)_2]X$ (X = ClO_4^- and halide ions) does not react with CO (Scheme I and II, procedure F and C′): the brown color does not disappear under CO atmosphere, the absorbance of the band at 440 nm being constant.

The isosbestic behavior was also observed by varying partial CO pressure. In Figure 4, we can determine the stoichiometry of the formation of a carbonyl complex (**3**). On the basis of eq 1–3, plots of log R vs. log P_{CO} were constructed for two wavelengths (440 and 480 nm). Figure 4B reveals a straight line, indicative of the validity of the treatment with eq 3. The value of n is 1, exhibiting the formation of monocarbonylated complex. The stoichiometry of 1 CO/2 Cu is surprising, reminding us of the active site of hemocyanin.[1,2] However, to determine whether a bond is formed with a single metal atom or both is beyond the treatment of the solution equilibrium. This is discussed in the following IR study. The coordination numbers and equilibrium constants for a series of Cu(I) complexes are listed in Table III.

A carbonyl adduct (**3**) can be isolated from a CO treated solution as a pale yellow microcrystalline material (ν_{CO} = 2066 cm^{-1}), which releases CO at room temperature. The solid $[CuCl(bpy)]_2$ reacts readily with CO at low temperature, and a carbonyl–decarbonyl cycle is repeated many times by varying temperature or passing nitrogen. The reversible reaction with CO in the solid state suggests that carbonyl adduct **3** is $Cu_2Cl_2(bpy)_2CO$ because it is highly unlikely that any of the ligands of **2** are dissociating upon the formation of the carbonyl adducts in the solid state. The value of 2066 cm^{-1} excludes the presence of the bridging CO group of which the ν_{CO} value is ca. 1900 cm^{-1} as has been found in $[Cu(en)CO]_2Cl_2$.[29] The evidence presented here provides two possible structures about the carbonyl adduct **3**: one is $[(bpy)CuCl_2Cu(bpy)(CO)]$ (structure A) having double-bridged halogen atoms, and another is $[Cl(bpy)CuClCu(bpy)(CO)]$ (structure B) having a single-bridged halogen atom. For a determination of which structure is most probable, IR spectra were observed in the region 400–250 cm^{-1}, where terminal MCl stretching frequencies are observed. In general,[30] bridging MCl stretching frequencies fall within 100–200 cm^{-1}, which are lower than terminal MCl stretching frequencies (>250 cm^{-1}). There are two terminal and bridging CuCl bonds in B. The IR spectrum of B would afford a terminal CuCl band in the region 400–250 cm^{-1}. The spectra of **3** observed here did not encounter the terminal CuCl stretching band in the region above 250 cm^{-1}, indicative of the absence of the terminal halide ion. Consequently, the five-coordinate CO adduct such as $[(bpy)CuCl_2Cu(bpy)(CO)]$ is most probable. A few five-coordinate carbonyl adducts[7,9,10] of Cu(I) complexes are known whose nearly square-planar structure permits its distortion upon carbonylation to a square-pyramidal coordination geometry. The value[7,9,10] of 2061–2068 cm^{-1} is in good agreement with that of 2066 cm^{-1} for the present carbonyl adduct **3**.

^1H NMR Spectra. In order to shed light on the solution structure of complex **3**, we measured ^1H NMR spectra for complexes **2** and **3**. Figure 5 shows the typical ^1H NMR spectra of bpy at −90 °C: above −70 °C, a chemical exchange rate between a bound and unbound bpy is fast enough and each proton signal is averaged to be a single braod band. When bpy is coordinated onto the Fe(II) ion,[20,31] small changes occur in the proton chemical shifts with exception of 3-H and 6-H protons, of which shifts are caused by the magnetic anisotropy of a neighboring ligand due to a characteristic geometry of $[Fe(bpy)_3]^{2+}$. In complex **2** studied here, no magnetic anisotropy of a neighboring ligand gives rise to 6-H proton due to T_d symmetry. Hence, the difference in the chemical shifts is small between bound and unbound bpy. In figure 5A, peak a_2 is assigned to a 4-H signal for complex **2** because this peak disappears when a 4,4′-dimethyl-2,2′-bipyridine (bpc) is used instead of bpy. Then, a_1 is ascribed to 5-H. 3-H and 6-H signals accidentally collapse each other to become a single peak. The ^1H NMR spectrum in Figure 5B is remarkably different from that for complex **2** (Figure 5A): all the signals[32] shift downfield in comparison with those for **2**. This indicates the formation of a carbonyl adduct (**3**). It is noteworthy in Figure 5C that ^1H signals between bound and unbound bpy are well separated: the peaks designated as b are ascribed to bpy in the CO adduct while well-resolved peaks are ^1H signals of the unbound bpy. The solution containing bpy and CuCl

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(29) Rucci, G.; Zanzottera, C.; Lachi, M. P.; Camia, M. *J. Chem. Soc., Chem. Commun.* **1971**, 652.

(30) (a) In our study, typical terminal CuCl stretching frequencies (340 cm^{-1}) were obtained for Cu^I(2,2′-biquinoline)Cl, which is very stable yellowish green crystalline. (b) The bridging CuCl did not appear in the region >250 cm^{-1}. Polymeric complexes $[M(py)_2Cl_2]_n$ (M = Co and Ni) afford the values of 170–190 cm^{-1}. Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1977.

(31) Castellano, S.; Günther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.

(32) The ^1H signals of the CO complex in Figure 5B, and C have not been completely assigned, because the chemical exchange rate is fast. Substitution of bpy with bpc made the b_2 signal disappear, indicating that b_2 is assigned to 4-H for bpy.

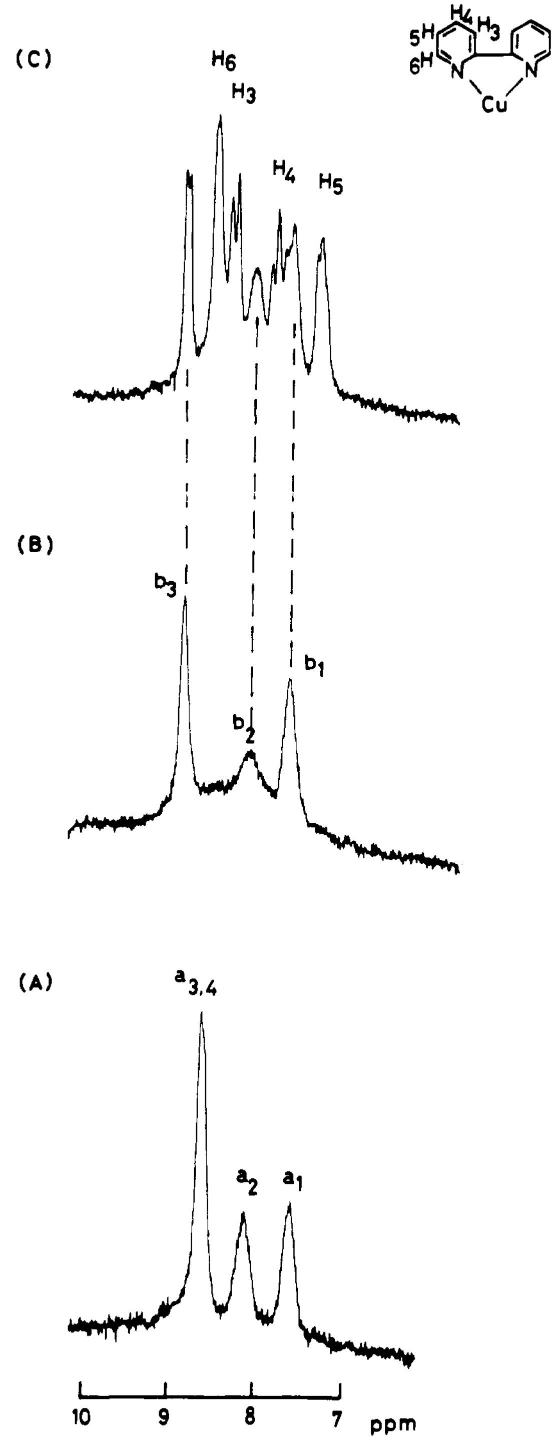

Figure 5. ^{1}H NMR spectra at −90 °C of a $(CD_3)_2CO$ solution of 1×10^{-3} M $[CuCl(bpy)]_2$: (A) $[bpy]_0/[CuCl]_0 = 1$, under an N_2 atmosphere; (B) $[bpy]_0/[CuCl]_0 = 1$, under a CO atmosphere; (C) $[bpy]_0/[CuCl]_0 = 2$, under a CO atmosphere. a_1–a_4 show the proton signals of bpy in $[CuCl(bpy)]_2$ and b_1–b_3 reveal those of the carbonyl adduct.

(just 1:1 ratio) exhibits no unbound bpy signals as shown in Figure 5B. Therefore, the addition of CO to complex **2** causes no dissociation of the coordinated bpy in complex **2**. Now, the carbonyl adduct in acetone solution may be $Cu_2Cl_2(bpy)_2CO$ as well as that in the solid state. The chemical shift data are listed in Table IV.

Solution Infrared Spectra. The solution infrared spectrum of adduct **3** (acetone, 1 atm CO) shows only a single peak attributable to coordinated CO ($\nu_{CO} = 2075$ cm^{-1}). This is almost consistent with the presence of a single carbonyl species in solution. The similarity between ν_{CO} in the solution (2075 cm^{-1}) and in the solid state (2066 cm^{-1}) leads to the conclusion that the solution species is also a five-coordinate carbonyl adduct **3**,[33] $[(bpy)CuCl_2Cu(bpy)(CO)]$.

Equilibrium Constants. As shown in Table III, the remarkable difference in the affinity for CO appears in halogeno derivatives $[CuX(bpy)]_2$. The equilibrium constants increase with the order Cl < Br < I. The effect of halogen has been found in the CO exchange reaction; for example, the exchange rate in $MnX(CO)_5$ (X = Cl, Br, and I)[27] follows the order Cl > Br > I. Generally, CO is a good π acceptor, and M–CO bonding is stabilized by π-back-bonding interaction. The trend has been accounted for by the electron density on Mn atom: the more electronegative Cl[34] decreases electron density on the Mn atom and promotes the dissociation of CO. In copper(I) complexes, electron density is also a significant factor to form a stable Cu–CO bonding.[10] In our complexes, their affinity for CO is also explained primarily by the inductive effect of the halide ion: the copper(I) atom becomes more positive in chloro derivatives than in iodo ones, indicating poor reactivity toward CO. Therefore, a Cu(I) atom in iodo complex is more attractive for CO than in chloro and bromo complexes.

Gagnê et al.[10] have pointed out that the four-coordinate precursor with square-planar configuration readily reacts with a fifth ligand to become a five-coordinate complex. On the other hand, the binuclear complexes $[CuXL]_2$ studied here may possess tetrahedral configuration about each Cu(I) atom (Figure 1). Upon addition of CO which causes the structural change of the precursor complexes from a tetrahedral to square-pyramidal configuration, a flexible ligand will be preferred because a rigid multidentate ligand may impose the structural restraint on the precursor complex. Bpy is expected to be available for a five-coordinate CO-complex in comparison with phen because of the flexible structure of bpy.[35] However, the CO-affinity of the phen derivative ($K_{CO} = 1.2$ atm^{-1}) exhibits only a slight difference from that of the bpy one ($K_{CO} = 1.3$ atm^{-1}), as shown in Table III. This is unexpected. The modification of the affinity for CO by phen is minor in the $[CuXL]_2$ complexes. Consequently, the flexibility of a bidentate ligand such as bpy is not necessarily important. These bidentate ligands participate in the stabilization of the Cu(I) oxidation state, which is associated with π-back-bonding interaction.

Now recall that $[Cu(bpy)_2]X$ (X = ClO_4^- and halide ions) does not react with CO[37] because a Cu(I) atom firmly binds two bpy to form a stable tetrahedral complex. In contrast, the binuclear complexes discussed above readily react with CO to give monocarbonyl adducts. The addition of CO to $[CuXL]_2$ presumably gives rise to the conformational change around at least one copper atom. Such a flexibility is associated with the specific structure of the present binuclear

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(33) ν_{CO} values of a carbonyl adduct under several conditions were obtained as follows: (i) the addition of CO to a crystalline compound (2066 cm^{-1}); (ii) the addition of CO to a solution of **2** and then precipitation of the carbonyl adduct (2065 cm^{-1}); (iii) the addition of CO to **2** in solution (2075 cm^{-1}).

(34) Electronegativity is a typical measure. For example, 3.0, 2.8, and 2.5 for Cl, Br, and I, respectively. Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(35) phen is a fairly rigid molecule as compared to bpy with a flexible C(2)–C(2′) bond concerning the rotation. In addition, the oxidation–reduction potentials[36] for bpy and phen complexes show that phen stabilizes the Cu(I) state rather than bpy possibly because phen has highly delocalized electronic structure whose π^* orbitals considerably contributes to π-back-bonding interaction. Phen might compete with CO, reducing the affinity of the copper(I) ion for CO.

(36) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.

(37) In ethanol, the absorbance slightly decreased under CO atmosphere, indicative of the formation of a carbonyl adduct. This is accounted for by the presence of the mono bpy complex [Cu(bpy)Cl(S)], which can react with CO to become [Cu(bpy)Cl(CO)] (Scheme I, procedure E′ and D′).

complexes having bridged halogen atoms. In these binuclear complexes, the charge-transfer interaction between Cu(I) and bpy is remarkably weakened upon the addition of CO, and consequently CO competes with bpy concerning the interaction with Cu(I) atom. Then, the bondings of Cu–L and Cu–CO are delicately balanced by the halide ions, as is illustrated by the variation of the CO affinity of halogeno derivatives in Table III. In this sense the bridged halogen atoms take an important role in the reaction with CO.

Finally, the equilibrium constants of [(bpy)$CuCl_2Cu$(bpy)CO] remarkably depend on solvent as shown in Table III. In a series of ketones, noncoordinating solvents, the following order is obtained: K(MP) > K(3-butanone) > K(acetone). In other words, the larger the bulk dielectric constant of solvent, the smaller the equilibrium constant. It is well-known[27] that the metal–CO bond has usually a low dipole moment and is electronically neutral. On this basis, the nonpolar media can be available for a tight Cu–CO bonding. Therefore, the solvent effect, regarded as a media effect, is characterized by bulk properties of the solvent such as the dielectric constant.

Conclusion. In summarizing the above results and discussion, the following conclusion is drawn. Binuclear $[CuXL]_2$ complexes reversibly react with CO. The resultant CO adducts are monocarbonylated five-coordinate complexes. Their stability is influenced by the several factors. (1) Effect of halide ions. This effect is primarily ascribed to their electronegativity. (2) The flexibility of the precursor complex to accept a square-pyramidal configuration. This flexibility is attributed to the specific binuclear structure having bridged halide ions. (3) Solvent effect on Cu–CO bonding. Nonpolar solvents promote the formation of Cu–CO bonding.

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Registry No. **2**, 77482-32-7; **3**, 77482-33-8; **4**, 39210-78-1; **5**, 74829-17-7; **6**, 77482-34-9; **7**, 77482-35-0; $[CuBr(bpy)]_2$, 77482-36-1; $[CuI(bpy)]_2$, 39210-77-0; $[CuCl(phen)]_2$, 77482-37-2; $[Cu(phen)_2]Cl$, 77482-38-3; $[Cu(phen)_2]ClO_4$, 23624-03-5; $[Cu(CH_3CN)_4]ClO_4$, 14057-91-1.

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Halogen Additions to Bis(diphenylphosphino)methane Complexes of Palladium. Interrelationships of Monomeric and Dimeric Complexes of Pd(II), Pd(I), and Pd(0)

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Addition of halogens (Cl_2, Br_2, I_2) and pentafluorophenyl disulfide to $Pd_2(dpm)_3$ (dpm = bis(diphenylphosphino)methane) proceeds stepwise, under stoichiometric control, to yield $Pd_2(dpm)_2X_2$ and $Pd(dpm)X_2$ as isolable products. Proton and phosphorus NMR data are reported for these complexes. During the oxidation of $Pd_2(dpm)_2X_2$ to $Pd(dpm)X_2$, $Pd_2(dpm)_2X_4$ is an intermediate which has been observed and identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Speculation on the mechanism of the conversion of $Pd_2(dpm)_2X_2$ to $Pd(dpm)X_2$ (bridging to chelating dpm) is offered.

Complexes with bridging bis(diphenylphosphino)methane (dpm) ligands have been reported for three different oxidation states of palladium: Pd(0) in $Pd_2(dpm)_3$,[1] Pd(I) in $Pd_2(dpm)_2X_2$ (X = halide or pseudohalide),[2] and Pd(II) in $Pd(dpm)X_2$.[3,4] Reactions interconverting these oxidation states must involve either ligand loss or the conversion of the dpm ligand from a bridging to a chelating form. While the versatility of bridging dpm ligands is known to facilitate a number of novel chemical reactions (metal–metal bond forming reactions,[5–7] metal–metal bond breaking reactions,[2,8–10] and reactions forming side-on bound bridging carbonyl[11] and isocyanide[12] ligands), little attention has been paid to reactions in which the nature or number of dpm ligands changes. In general, conditions have been found where reactions involving dinuclear, doubly bridged complexes give dimeric products in high yield and with little evidence for monomeric or more highly polymerized side products. However, we have been aware for some time that certain reactions of dinuclear dpm complexes proceed to give mononuclear products. This is particularly true when elevated temperatures (>50 °C) are used. We have reported that the oxidation of dimeric $Rh_2(dpm)_2(CN\text{-}n\text{-}Bu)_4{}^{2+}$ by some disulfides produces monomeric Rh(III) complexes rather than dimeric Rh(II) species like those which are formed by the corresponding oxidation by halogens.[13] The specific reaction paths involved in depolymerization or polymerization for dpm complexes have not as yet been explored.

The relationship between Pd(I) and Pd(II) dpm complexes is a case where depolymerization is important. Pd(I)–dpm complexes of the type $Pd_2(dpm)_2X_2$ (X = anionic ligand, usually a halide or pseudohalide) possess the structure **1** in which two nearly planar metal centers are joined through a direct Pd–Pd bond. This structural type has been established through crystallographic studies of $Pd_2(dpm)_2Br_2$[14] and $Pd_2(dpm)_2Cl(SnCl_3)$[15] and the isoelectronic Pt(I) complex Pt_2-

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