the electrical charge of the redox-active metal ions. In particular, it has been shown that its effective value varies with the nature of the metal and with its stereochemical arrangement. Moreover, the bulk value of the dielectric constant of the medium is absolutely not appropriate to describe the shielding effect exerted by the solvational molecules. In particular, in strongly saline solutions, the ions of the so-called "inert electrolyte" may substantially modify the solvation state of the dimetallic system and seriously affect its redox behavior. The only parameter of Coulomb's law whose role seems to be accounted for, in a quantitative sense, is the distance between metal centers. Due to the stretched arrangement of the joining chain, its value can be calculated on the basis of molecular models.

Acknowledgment. Financial support by the Italian Ministry of Public Education (MPI 40%) is gratefully acknowledged.

Registry No. **1**, 295-37-4; **2**, 110078-38-1; **2a**, 110078-39-2; **3**, 110078-40-5; **3a**, 110078-41-6; **4**, 110078-42-7; **4a**, 110078-43-8; **4b**, 110078-48-3; **5**, 110078-44-9; **5a**, 110078-45-0; **6**, 110078-46-1; **6a**, 110078-47-2; **7**, 104395-69-9; $[Cu_2(\mathbf{2})](ClO_4)_4$, 110095-31-3; $[Cu_2(\mathbf{2})]^{5+}$, 110095-60-8; $[Cu_2(\mathbf{2})]^{6+}$, 110095-50-6; $[Cu_2(\mathbf{3})](ClO_4)_4$, 110095-33-5; $[Cu_2(\mathbf{3})]^{5+}$, 110095-61-9; $[Cu_2(\mathbf{3})]^{6+}$, 110095-51-7; $[Cu_2(\mathbf{4})](ClO_4)_4$, 110095-35-7; $[Cu_2(\mathbf{4})]^{5+}$, 110095-62-0; $[Cu_2(\mathbf{4})]^{6+}$, 110095-52-8; $[Cu_2(\mathbf{5})](ClO_4)_4$, 110095-37-9; $[Cu_2(\mathbf{5})]^{5+}$, 110095-63-1; $[Cu_2(\mathbf{5})]^{6+}$, 110095-53-9; $[Cu_2(\mathbf{6})](ClO_4)_4$, 110095-39-1; $[Cu_2(\mathbf{6})]^{5+}$, 110095-64-2; $[Cu_2(\mathbf{6})]^{6+}$, 110095-54-0; $[Ni_2(\mathbf{2})](ClO_4)_4$, 110095-41-5; $[Ni_2(\mathbf{2})]^{5+}$, 110095-65-3; $[Ni_2(\mathbf{2})]^{6+}$, 110095-55-1; $[Ni_2(\mathbf{3})](ClO_4)_4$, 110095-43-7; $[Ni_2(\mathbf{3})]^{5+}$, 110095-66-4; $[Ni_2(\mathbf{3})]^{6+}$, 110095-56-2; $[Ni_2(\mathbf{4})](ClO_4)_4$, 110095-45-9; $[Ni_2(\mathbf{4})]^{5+}$, 110095-67-5; $[Ni_2(\mathbf{4})]^{6+}$, 110095-57-3; $[Ni_2(\mathbf{5})](ClO_4)_4$, 110095-47-1; $[Ni_2(\mathbf{5})]^{5+}$, 110095-68-6; $[Ni_2(\mathbf{5})]^{6+}$, 110095-58-4; $[Ni_2(\mathbf{6})](ClO_4)_4$, 110095-49-3; $[Ni_2(\mathbf{6})]^{5+}$, 110095-69-7; $[Ni_2(\mathbf{6})]^{6+}$, 110095-59-5; $TsOCH_2CH_2OTs$, 6315-52-2; $TsOCH_2CH_2CH_2OTs$, 5469-66-9; TsCl, 98-59-9; $BrCH_2$-*m*-C_6H_4–CH_2Br, 626-15-3; $BrCH_2$-*p*-C_6H_4–CH_2Br, 623-24-5; $COCl(CH_2)_2COCl$, 543-20-4.

Supplementary Material Available: A table containing melting points and analytical data (C, H, N) of the bis(macrocycles) **2–4** and of their protected precursors (1 page). Ordering information is given on any masthead page.

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Lewis-Base Adducts of Group 11 Metal(I) Compounds. 32. Steric Effects in the 2:1 Adducts of (2-Methylphenyl)diphenylphosphine with Copper(I) Halides

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Received April 1, 1987

Solid-state ^{31}P NMR spectra, far-infrared spectra, and single-crystal X-ray structure determinations have been recorded for (2-methylphenyl)diphenylphosphine (PPh_2-*o*-tol) and its mononuclear 2:1 adducts with copper(I) halides, $(PPh_2\text{-}o\text{-tol})_2CuX$. The solid state ^{31}P NMR spectrum of the ligand shows a single sharp resonance at −18 ppm with respect to 85% H_3PO_4. The spectra of the 2:1 adducts show two sets of overlapping asymmetric quartets for the chloride and bromide and a single broad quartet for the iodide, indicating the presence of at least two crystallographically distinct ligands in the first two compounds and one in the third. Average chemical shift values (ppm) are as follows: Cl, −11; Br, −11; I, −15. The asymmetry in the line spacing for each quartet is consistent with a trigonal coordination geometry around the copper atom. Far-infrared spectra of each of the metal complexes in the range 50–400 cm^{-1} show strong bands that are assigned to terminal metal–halogen stretching vibrations: Cu–Cl, 290 cm^{-1}; Cu–Br, 220 cm^{-1}; Cu–I, 200 cm^{-1}. The parent ligand crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.713$ (5) Å, $b = 8.726$ (5) Å, $c = 16.573$ (6) Å, $\beta = 90.77$ (3)°, and $Z = 4$. All three copper structures crystallize in the monoclinic space group $C2/c$. The Cl and Br structures are isomorphous with one complete molecule of $(PPh_2\text{-}o\text{-tol})_2CuX$ comprising the asymmetric unit. For X = Cl, $a = 22.413$ (15) Å, $b = 16.034$ (4) Å, $c = 19.092$ (2) Å, $\beta = 107.04$ (4)°, and $Z = 8$; for X = Br, $a = 22.348$ (7) Å, $b = 16.033$ (8) Å, $c = 19.526$ (5) Å, $\beta = 108.73$ (2)°, and $Z = 8$. However, for X = I, $a = 18.665$ (5) Å, $b = 10.006$ (2) Å, $c = 19.764$ (5) Å, $\beta = 115.29$ (2)°, and $Z = 4$, with the two ligands related by symmetry and the Cu–I bond sited on the 2-fold rotation axis. For X = Cl, Cu–P, Cu–P, Cu–X, and P–Cu–P = 2.241 (2) Å, 2.257 (2) Å, 2.205 (2) Å, and 126.96 (7)° respectively; for X = Br, the values are 2.240 (2) Å, 2.255 (2) Å, 2.336 (1) Å, and 127.89 (7)°, respectively; and for X = I, Cu–P, Cu–I, and P–Cu–P = 2.255 (1) Å, 2.507 (1) Å, and 126.36 (7)°, respectively. Both Cu–P and Cu–X distances are similar to the corresponding values for $(PPh_3)_2CuX$ compounds. However, as a consequence of changes in steric profile, the conformational structure of each ligand about the Cu–P bonds with respect to Cu–X is significantly different.

Introduction

Reaction of copper(I) halides, CuX, with tertiary organophosphine bases, PR_3, gives a wide range of products of variable stoichiometry and molecular structure. Most structural studies have been reported for compounds of 1:1 stoichiometry, $[PR_3CuX]_n$, and here the stellaquadrangula[2] or "cubane" structure is most common, crystallographic data being reported for a wide range of bases with differing steric and electronic characteristics including PEt_3 with X = Cl,[3] Br,[3] and I;[4] $PMePh_2$ with X = I;[5] PPh_3 with X = Cl,[6] Br,[7] and I,[8] and P(*t*-Bu)$_3$ with X = Br.[9] For PPh_3 and X = Br and I, a change of solvent results in the crystallization of the alternative "step" tetramer.[10] For the ligands, $P(chx)_3$ (chx = cyclohexyl) with X = Cl and $P(mes)_3$ (mes = mesityl) with X = Br, dimeric $[PR_3CuX]_2$[11] and monomeric $[PR_3CuX]$[12] structures, respectively, are obtained. By contrast,

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structural data for compounds with ligand to CuX stoichiometric ratios greater than one are scarce. $PPhH_2$[13] and $PMePh_2$[14] with X = I have been shown to crystallize as 2:1 dimers, $(PR_3)_2CuX_2Cu(PR_3)_2$ and 3:1 monomers have been reported for $PMePh_2$ with X = Cl[14] and for PPh_3 with X = Cl,[14,15] Br,[15], and I.[15] PPh_3 yields, under special conditions, a 2:1 monomer, L_2CuX, with X = Cl,[16] Br,[17] and I,[16] the more common product from solutions of this stoichiometry being the structurally unique 1.5:1 dimer, $(PR_3)_2CuX_2Cu(PR_3)$.[10]

The generalization has often been made that the molecular structure for a given complex within this series is controlled primarily by the size of the ligand, which is usually defined in terms of the Tolman cone angle.[18] While this is undoubtedly a good first approximation, inconsistencies in the structural results exist. For example, despite its larger cone angle, $P(t\text{-}Bu)_3CuBr$ is tetrameric while $P(chx)_3CuCl$ is dimeric; i.e. the ligand profile[18,19] as well must be taken into account in predicting structural properties. The structural chemistry of $[(PPh_3)CuX]_4$,[6-8] $[(PPh_3)_3(CuX)_2]$,[10] and $[(PPh_3)_3CuX]$[15] has indicated that solvent interactions may also be important in stabilizing different molecular geometries in this system, and our recent work on the structural chemistry of the monomeric $(PPh_3)_2CuX$ system[16] has shown as well that halide–phenyl *o*-hydrogen interactions also may play a role.

Given this array of results, it seemed likely that quite small ortho modifications on the ligand could substantially affect the structure and chemical reactivity of the compounds obtained and to test this we prepared the ligand (2-methylphenyl)diphenylphosphine, PPh_2-*o*-tol, and reacted it with CuCl, CuBr, and CuI in a 2:1 molar ratio in acetonitrile solution to give white crystalline precipitates. Chemical analyses on the compounds obtained showed that the sole products had the stoichiometric formula $(PPh_2\text{-}o\text{-}tol)_2CuX$ and both solid-state ^{31}P NMR and far-infrared spectroscopic data strongly supported the molecular structure of each as monomeric rather than dimeric. This was subsequently confirmed by single-crystal X-ray structure determinations, and the results of this work are presented here, together with an analysis of the effects of the steric profile of the ligand and X···H interactions on the molecular structure.

Experimental Section

Preparation of PPh_2-*o*-tol. A solution of 60 mL of chlorodiphenylphosphine in 60 mL of tetrahydrofuran was added to 150 mL of a 2.03 M solution of $CH_3C_6H_4MgCl$ in tetrahydrofuran at −78 °C. The mixture was warmed to room temperature and left to stand for 2 h; the solvent was removed in vacuo and the residue extracted with dichloromethane and then concentrated to a pale brown oil. A 200-mL aliquot of ethanol was added and the solution cooled to −30 °C to yield white crystals, mp 69–71 °C (lit.[20] 66–67 °C). Anal. Calcd for $C_{19}H_{17}P$: C, 82.6; H, 6.2. Found: C, 82.1; H, 6.3.

Preparation of $(PPh_2\text{-}o\text{-}tol)_2CuX$. All three complexes were prepared similarly. A 0.001-mol sample of the copper halide was dissolved in degassed acetonitrile, and slightly more than 0.002 mol of the ligand was added. White crystalline precipitates formed immediately. Dissolution by heating followed by slow cooling gave clear colorless crystals of the compounds. Mp: X = Cl, 209–215 °C; X = Br, 224–228 °C; X = I, 218–222 °C. Anal. Calcd for $C_{38}H_{34}CuClP_2$: C, 70.0; H, 5.3. Found: C, 70.4; H, 5.4. Calcd for $C_{38}H_{34}CuBrP_2$: C, 65.6; H, 4.9. Found: C, 65.2; H, 5.0. Calcd for $C_{38}H_{34}CuIP_2$: C, 61.4; H, 4.6. Found: C, 61.6; H, 4.7.

Spectroscopy. Solid-state ^{31}P spectra of the compounds were obtained at room temperature on a Bruker CXP-300 spectrometer at 121.47 MHz using ^1H–^{31}P cross-polarization with radiofrequency fields of 8 and 20 G, respectively, as described previously.[7] Chemical shift data were referenced to 85% H_3PO_4 via solid triphenylphosphine ($\delta(PPh_3)$= −9.9 ppm) (Figure 1, Table I).

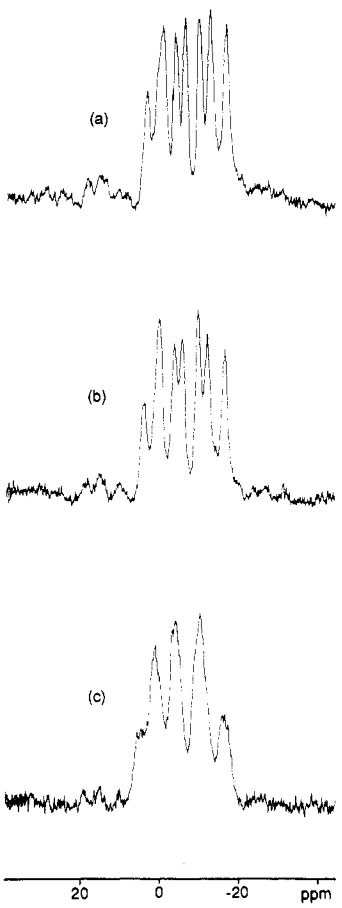

Figure 1. ^{31}P solid-state NMR spectra: (a) $(PPh_2\text{-}o\text{-}tol)_2CuCl$; (b) $(PPh_2\text{-}o\text{-}tol)_2CuBr$; (c) $(PPh_2\text{-}o\text{-}tol)_2CuI$.

Table I. Solid-State ^{31}P NMR Data for $(PPh_2\text{-}o\text{-}tol)_2CuX$ Compounds[a]

	chem shifts					line spacing/10^3 Hz			
X	δ_1	δ_2	δ_3	δ_4	$\langle\delta\rangle$	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_{ij}$
Cl	6	−2	−12	−24	−8	0.90	1.25	1.40	0.50
	1	−7	−18	−32	−14	0.95	1.30	1.60	0.65
Br	7	−2	−11	−23	−7	1.00	1.15	1.40	0.40
	1	−8	−18	−31	−14	1.05	1.30	1.55	0.50
I	1	−8	−20	−31	−15	1.10	1.40	1.40	0.30

[a] δ_i are chemical shift values with respect to 85% H_3PO_4 via PPh_3 (−9.9 ppm). Where peaks overlap, the δ value quoted is an estimate only. $\langle\delta\rangle$ is the average chemical shift for each quartet. $\Delta\nu_i$ is the line spacing between each of the four peaks of each quartet. $\Delta\nu_{ij} = \Delta\nu_i(\max) - \Delta\nu_i(\min)$ is defined here as an estimate of the asymmetry parameter of the quartet.

Far-infrared spectra were recorded at ca. 298 and 125 K as petroleum jelly mulls between polyethylene plates on a Grubb-Parsons Mk II cube interferometer interfaced to an IBM PC microcomputer and were calibrated against the spectrum of water vapor (Figure 2).

Structure Determinations. A summary of crystal data is presented in Table II. Unique data sets were measured to the specified $2\theta_{\max}$ limits on specimens mounted in capillaries by using Syntex $P\bar{1}$ and ENRAF Nonius CAD-4 four-circle diffractometers (monochromatic Mo Kα radiation sources, λ = 0.7106$_9$ Å) in conventional $2\theta/\theta$ scan mode, at 295 K. N independent reflections were measured, N_o with $I > 2{,}3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement with statistical weights after solution of the structures by the heavy atom method. $(x, y, z, U_{iso})_H$ were included at idealized values for the ligand, chloride, and bromide complexes. $(x, y, z)_H$ were refined for the iodide complex. Residuals on $|F|$ at convergence were conventional R and R'. Each structure refined smoothly in the chosen space group with no

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Table II. Summary of Crystal Data for PPh$_2$-*o*-tol and (PPh$_2$-*o*-tol)$_2$CuX

	PPh$_2$-*o*-tol	(PPh$_2$-*o*-tol)$_2$CuCl	(PPh$_2$-*o*-tol)$_2$CuBr	(PPh$_2$-*o*-tol)$_2$CuI
formula	$C_{19}H_{17}P$	$C_{38}H_{34}CuClP_2$	$C_{38}H_{34}CuBrP_2$	$C_{38}H_{34}CuIP_2$
fw	276.3	651.7	696.1	743.1
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$
a/Å	10.713 (5)	22.413 (15)	22.348 (7)	18.665 (5)
b/Å	8.726 (5)	16.034 (4)	16.033 (8)	10.006 (2)
c/Å	16.573 (6)	19.092 (2)	19.526 (5)	19.764 (5)
β/deg	90.77 (3)	107.04 (4)	108.73 (2)	115.29 (2)
V/Å^3	1549 (1)	6560 (2)	6626 (2)	3337 (2)
Z	4	8	8	4
D_m/g cm^{-3}	1.17 (2)	1.30 (2)	1.41 (2)	1.50 (2)
D_c/g cm^{-3}	1.18	1.32	1.40	1.48
F(000)	584	2704	2848	1496
μ_{Mo}/cm^{-1}	1.74	9.0	20.9	17.5
cryst size/mm	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.25	0.24 × 0.16 × 0.16	0.30 × 0.20 × 0.10
abs cor	no	no	analytical	no
A^*_{min}; A^*_{max}			1.32; 1.39	
$2\theta_{max}$/deg	45	45	45	50
N	2036	2904	4234	2957
N_o	1066	2285	2895	2002
condition	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
ind var	181	380	380	243
R	0.061	0.044	0.059	0.033
R'	0.082	0.040	0.034	0.034

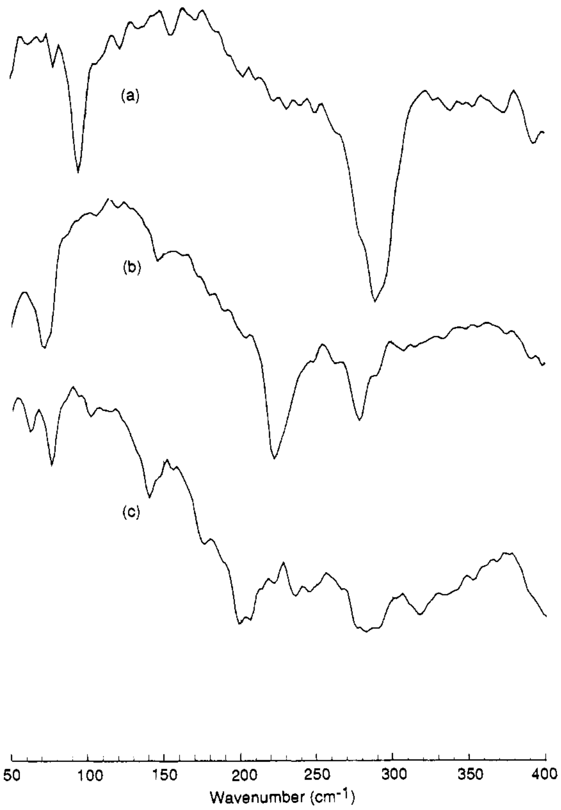

Figure 2. Far-infrared spectra: (a) (PPh$_2$-*o*-tol)$_2$CuCl; (b) (PPh$_2$-*o*-tol)$_2$CuBr; (c) (PPh$_2$-*o*-tol)$_2$CuI.

Table III. Non-Hydrogen Atom Coordinates for PPh$_2$-*o*-tol

atom	x	y	z
P	0.6654 (3)	0.2422 (4)	0.4167 (2)
C(11)	0.805 (1)	0.131 (2)	0.3911 (7)
C(12)	0.819 (1)	−0.009 (2)	0.4282 (8)
C(121)	0.734 (2)	−0.074 (2)	0.4887 (8)
C(13)	0.916 (2)	−0.098 (2)	0.4101 (9)
C(14)	1.009 (2)	−0.051 (2)	0.3565 (10)
C(15)	0.994 (1)	0.090 (2)	0.3192 (8)
C(16)	0.890 (1)	0.180 (1)	0.3374 (8)
C(21)	0.721 (1)	0.349 (1)	0.5063 (6)
C(22)	0.626 (1)	0.400 (1)	0.5596 (8)
C(23)	0.665 (2)	0.483 (2)	0.6286 (8)
C(24)	0.789 (2)	0.512 (2)	0.6449 (8)
C(25)	0.873 (1)	0.460 (2)	0.5931 (9)
C(26)	0.841 (1)	0.378 (2)	0.5249 (8)
C(31)	0.666 (1)	0.392 (2)	0.3390 (7)
C(32)	0.624 (1)	0.348 (1)	0.2623 (8)
C(33)	0.614 (1)	0.453 (2)	0.2011 (8)
C(34)	0.644 (1)	0.603 (1)	0.2146 (8)
C(35)	0.685 (1)	0.648 (1)	0.2901 (9)
C(36)	0.697 (1)	0.544 (2)	0.3520 (7)

anomalies with respect to features such as thermal envelopes or disorder. Neutral-atom complex scattering factors were used.[21] No significant extinction effects were observed. Computation used the XTAL83 program system[22] implemented by S. R. Hall on a Perkin-Elmer 3240 computer, and the APPLECRYST program package, written by C. H. L. Kennard for an Apple IIe microcomputer. Non-hydrogen atom coordinates are given in Tables III–VI; the atom-labeling scheme adopted for the PPh$_2$-*o*-tol ligands is as described in ref 15. The ortho carbon atoms, C(*l*m2) (*m* = ring number 1, 2, or 3) are outside the PC$_3$ pyramid. Pertinent geometric parameters are given in Tables VII and VIII.

Results and Discussion

Solid-State ^{31}P NMR Spectra. The solid-state CPMAS ^{31}P NMR spectrum of the ligand gives a single sharp line at −18 ppm with respect to 85% H_3PO_4 which is ca. 5 ppm upfield from the reported solution value of −13 ppm, recorded in CH_2Cl_2 solution.[20] The spectra of the complexes show broad signals of relatively low intensity. The chloride and bromide spectra can be resolved into two overlapping quartets whereas the iodide is better described as consisting of one broad quartet only (Figure 1). These results are consistent with the crystallographic data. Although all three complexes crystallize in space group *C*2/*c*, the asymmetric units of the isomorphous chloride and bromide structures contain the entire molecule with each PPh$_2$-*o*-tol ligand adopting distinctly different conformational structures (Table VII), whereas for the iodide structure the two ligands are related by a 2-fold rotation symmetry operation, the rotation axis lying along the Cu–I vector.

The average chemical shift values for each compound of Cl = −11, Br = −11, and I = −15 ppm represent a 3–7 ppm downfield shift from that of the parent ligand, a similar downfield shift also being found for (PPh$_3$)$_2$CuX.[16] More compelling evidence of the structural similarities between the two series of compounds is, however, the magnitude and asymmetry of the line spacing with the magnitude varying from a value of 0.9 × 10^3 Hz for the

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Table IV. Non-Hydrogen Atom Coordinates for (PPh$_2$-*o*-tol)$_2$CuCl

atom	*x*	*y*	*z*
Cu	0.26108 (3)	0.43254 (5)	0.10348 (4)
Cl	0.28323 (8)	0.3245 (1)	0.1780 (1)
P(1)	0.33933 (7)	0.5152 (1)	0.09517 (8)
P(2)	0.15789 (7)	0.4583 (1)	0.05870 (8)
C(111)	0.4159 (2)	0.4680 (4)	0.1106 (3)
C(112)	0.4285 (3)	0.3941 (4)	0.1476 (3)
C(113)	0.4876 (3)	0.3582 (5)	0.1615 (4)
C(114)	0.5333 (3)	0.3964 (5)	0.1402 (4)
C(115)	0.5213 (3)	0.4686 (5)	0.1025 (5)
C(116)	0.4626 (3)	0.5046 (4)	0.0867 (4)
C(121)	0.3508 (2)	0.5929 (3)	0.1676 (3)
C(122)	0.3000 (3)	0.6289 (4)	0.1802 (3)
C(123)	0.3062 (3)	0.6866 (4)	0.2356 (4)
C(124)	0.3619 (3)	0.7071 (5)	0.2792 (4)
C(125)	0.4141 (3)	0.6727 (6)	0.2672 (5)
C(126)	0.4086 (3)	0.6149 (5)	0.2114 (4)
C(131)	0.3298 (2)	0.5755 (4)	0.0121 (3)
C(132)	0.3147 (2)	0.5350 (4)	−0.0554 (3)
C(1321)	0.3056 (3)	0.4419 (4)	−0.0632 (3)
C(133)	0.3073 (3)	0.5826 (5)	−0.1191 (3)
C(134)	0.3138 (3)	0.6670 (5)	−0.1157 (4)
C(135)	0.3282 (3)	0.7075 (4)	−0.0498 (4)
C(136)	0.3360 (3)	0.6619 (4)	0.0132 (4)
C(211)	0.1044 (2)	0.3711 (3)	0.0531 (3)
C(212)	0.1124 (3)	0.2978 (4)	0.0171 (3)
C(2121)	0.1654 (3)	0.2870 (5)	−0.0163 (4)
C(213)	0.0699 (3)	0.2341 (4)	0.0122 (4)
C(214)	0.0200 (3)	0.2408 (4)	0.0394 (4)
C(215)	0.0128 (3)	0.3117 (4)	0.0756 (3)
C(216)	0.0541 (3)	0.3767 (4)	0.0822 (3)
C(221)	0.1362 (2)	0.5321 (3)	0.1197 (3)
C(222)	0.1642 (3)	0.5251 (4)	0.1933 (3)
C(223)	0.1517 (3)	0.5804 (5)	0.2418 (4)
C(224)	0.1107 (3)	0.6444 (5)	0.2164 (4)
C(225)	0.0814 (3)	0.6520 (4)	0.1433 (4)
C(226)	0.0937 (3)	0.5962 (4)	0.0942 (3)
C(231)	0.1296 (2)	0.5061 (4)	−0.0313 (3)
C(232)	0.1628 (2)	0.5714 (4)	−0.0495 (3)
C(233)	0.1430 (3)	0.6083 (4)	−0.1185 (3)
C(234)	0.0898 (3)	0.5799 (5)	−0.1686 (3)
C(235)	0.0565 (3)	0.5147 (5)	−0.1523 (3)
C(236)	0.0760 (3)	0.4791 (4)	−0.0835 (3)

Table V. Non-Hydrogen Atom Coordinates for (PPh$_2$-*o*-tol)$_2$CuBr

atom	*x*	*y*	*z*
Cu	0.26251 (4)	0.43173 (5)	0.10117 (4)
Br	0.28728 (4)	0.31966 (6)	0.18186 (5)
P(1)	0.34118 (8)	0.5150 (1)	0.09520 (9)
P(2)	0.15765 (8)	0.4557 (1)	0.05665 (9)
C(111)	0.4189 (3)	0.4706 (4)	0.1105 (3)
C(112)	0.4358 (3)	0.3990 (4)	0.1490 (3)
C(113)	0.4962 (3)	0.3653 (5)	0.1642 (4)
C(114)	0.5391 (3)	0.4030 (5)	0.1416 (4)
C(115)	0.5237 (3)	0.4730 (5)	0.1025 (4)
C(116)	0.4637 (3)	0.5078 (5)	0.0863 (4)
C(121)	0.3534 (3)	0.5907 (4)	0.1672 (3)
C(122)	0.3023 (3)	0.6235 (4)	0.1810 (4)
C(123)	0.3063 (3)	0.6796 (5)	0.2358 (4)
C(124)	0.3643 (3)	0.7034 (5)	0.2772 (4)
C(125)	0.4155 (3)	0.6733 (6)	0.2649 (5)
C(126)	0.4098 (3)	0.6173 (5)	0.2101 (4)
C(131)	0.3294 (2)	0.5766 (4)	0.0131 (3)
C(132)	0.3132 (3)	0.5366 (4)	−0.0539 (3)
C(1321)	0.3048 (3)	0.4451 (4)	−0.0632 (3)
C(133)	0.3045 (3)	0.5856 (5)	−0.1153 (3)
C(134)	0.3107 (3)	0.6699 (5)	−0.1115 (4)
C(135)	0.3245 (4)	0.7089 (4)	−0.0460 (4)
C(136)	0.3350 (3)	0.6627 (4)	0.0164 (4)
C(211)	0.1049 (2)	0.3681 (4)	0.0508 (3)
C(212)	0.1117 (3)	0.2955 (4)	0.0142 (3)
C(2121)	0.1623 (3)	0.2856 (5)	−0.0192 (4)
C(213)	0.0685 (3)	0.2315 (4)	0.0088 (3)
C(214)	0.0197 (3)	0.2376 (4)	0.0357 (4)
C(215)	0.0133 (3)	0.3082 (4)	0.0725 (3)
C(216)	0.0558 (3)	0.3727 (4)	0.0794 (3)
C(221)	0.1369 (3)	0.5274 (4)	0.1171 (3)
C(222)	0.1633 (3)	0.5156 (4)	0.1912 (3)
C(223)	0.1501 (3)	0.5697 (5)	0.2390 (3)
C(224)	0.1120 (3)	0.6376 (4)	0.2144 (4)
C(225)	0.0851 (3)	0.6492 (4)	0.1424 (4)
C(226)	0.0974 (3)	0.5951 (4)	0.0929 (3)
C(231)	0.1266 (3)	0.5035 (4)	−0.0322 (3)
C(232)	0.1605 (3)	0.5687 (4)	−0.0492 (3)
C(233)	0.1392 (3)	0.6059 (4)	−0.1170 (3)
C(234)	0.0850 (3)	0.5791 (5)	−0.1672 (3)
C(235)	0.0517 (3)	0.5153 (4)	−0.1506 (3)
C(236)	0.0713 (3)	0.4783 (4)	−0.0837 (3)

Table VI. Non-Hydrogen Atom Coordinates for (PPh$_2$-*o*-tol)$_2$CuI

atom	*x*	*y*	*z*
Cu	0	0.20764 (8)	$^1/_4$
I	0	−0.04289 (5)	$^1/_4$
P	0.02162 (7)	0.3093 (1)	0.35886 (6)
C(11)	0.0598 (3)	0.2140 (5)	0.4465 (2)
C(12)	0.1322 (3)	0.1458 (5)	0.4692 (3)
C(121)	0.1789 (3)	0.1456 (7)	0.4231 (3)
C(13)	0.1608 (4)	0.0777 (6)	0.5365 (3)
C(14)	0.1205 (4)	0.0764 (7)	0.5808 (3)
C(15)	0.0496 (4)	0.1415 (7)	0.5587 (3)
C(16)	0.0186 (3)	0.2108 (5)	0.4910 (3)
C(21)	−0.0772 (3)	0.3647 (5)	0.3448 (2)
C(22)	−0.1390 (3)	0.2750 (6)	0.3104 (3)
C(23)	−0.2164 (3)	0.3136 (7)	0.2936 (4)
C(24)	−0.2328 (3)	0.4389 (7)	0.3100 (3)
C(25)	−0.1724 (3)	0.5286 (6)	0.3435 (3)
C(26)	−0.0940 (3)	0.4917 (5)	0.3611 (3)
C(31)	0.0802 (3)	0.4625 (5)	0.3849 (2)
C(32)	0.0947 (3)	0.5308 (5)	0.3312 (3)
C(33)	0.1310 (3)	0.6545 (6)	0.3466 (3)
C(34)	0.1561 (3)	0.7073 (6)	0.4175 (3)
C(35)	0.1449 (3)	0.6386 (6)	0.4721 (3)
C(36)	0.1072 (3)	0.5162 (5)	0.4563 (2)

spacing between the low-field lines to 1.6 × 10^3 Hz between the high-field lines, which are, within experimental error, the same as corresponding values for (PPh$_3$)$_2$CuX.

Infrared Spectra. The infrared spectra in the region 50–400 cm^{-1} of each of the three metal complexes, recorded at ca. 125 K, are illustrated in Figure 2. The spectrum of the ligand shows weak bands at 210, 235, and 275 cm^{-1} that are essentially unchanged on coordination with the metal. In the spectra of the three complexes, strong bands are observed at 290, 220, and 200 cm^{-1} for the Cl, Br, and I compounds, respectively. For comparison, the spectra of monomeric (PPh$_3$)$_2$CuX compounds show similar bands at 290, 220, and 185 cm^{-1}, these being assigned to the terminal M–X stretching vibrations,[16] and a parallel assignment in the present complexes seems reasonable.

Crystal Structures. The parent ligand exists as discrete molecules with the *o*-methyl group on the same side of the ligand as the lone pair on the phosphorus atom (Figure 3). The P–C distances of 1.84 (1), 1.84 (1), and 1.83 (1) Å (⟨1.84 (1) Å⟩) are very similar to those of the two "parent" ligands: for PPh$_3$,[23] 1.822 (5), 1.831 (5), and 1.831 (5) Å (⟨1.83 (1) Å⟩); for P(*o*-tol)$_3$,[24] 1.837 (2), 1.836 (2), 1.836 (2), 1.837 (2), 1.836 (2), and 1.830 (2) Å (⟨1.83 (1) Å⟩). The same is true for C–P–C angles 101.2 (6), 101.5 (5), and 101.8 (6)° (⟨101.5 (2)°⟩): for PPh$_3$, 103.6 (2), 102.1 (2), and 103.3 (2)° (⟨103.0 (5)°⟩); for P(*o*-tol)$_3$ molecule 1, 101.9 (1), 103.1 (1), and 103.4 (1)°; for P(*o*-tol)$_3$ molecule 2, 101.6 (1), 102.7 (1), and 102.9 (1)° (⟨102.6 (3)°⟩). (Standard errors are calculated from the available range of distances and angles.) In these P(aryl)$_3$ compounds, the angles of intersection between the normals to the planes of the phenyl rings approach 90° in order to minimize the packing energy in these structures.[25] For example: PPh$_3$, 84, 77, and 78°; PPh$_2$-*o*-tol,

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Table VII. Conformational Angles (deg) for Mononuclear $(PR_3)_2CuX$ Compounds

		X–Cu–P(*l*)–C(*lm*1)			Cu–P(*l*)–C(*lm*1)–C(*lm*2)		
compd	*l*	*m* = 1	*m* = 2	*m* = 3	*m* = 1	*m* = 2	*m* = 3
$(PPh_2$-*o*-tol$)_2CuCl$	1	−30	87	−155	20	43	55
	2	26	−92	151	53	37	43
$(PPh_2$-*o*-tol$)_2CuBr$	1	−32	84	−158	23	40	56
	2	28	−89	153	54	43	42
$(PPh_2$-*o*-tol$)_2CuI$	1	−14	103	−143	−58	−43	−15
$(PPh_3)_2CuCl$[a]	1	2	119	−121	−37	−53	−38
	2	10	−116	127	−17	−51	−63
$(PPh_3)_2CuBr$[a]	1	−1	117	−124	−39	−53	−39
	2	13	−113	130	−19	−50	−63
$(PPh_3)_2CuI$[a]	1	5	−118	124	−35	−37	−61

[a] Reference 16.

Table VIII. Core Geometries for $(PPh_2$-*o*-tol$)_2CuX$ and $(PPh_3)_2CuX$

compd	M–P/Å	M–X/Å	P–M–P/ deg	P–M–X/ deg
$(PPh_2$-*o*-tol$)_2CuCl$	2.241 (2)	2.205 (2)	126.96 (7)	118.55 (7)
	2.257 (2)			113.61 (7)
$(PPh_3)_2CuCl{\cdot}0.5C_6H_6$[a]	2.260 (2)	2.208 (2)	125.48 (7)	120.74 (6)
	2.272 (2)			113.76 (7)
$(PPh_2$-*o*-tol$)_2CuBr$	2.240 (2)	2.336 (1)	127.89 (7)	118.25 (6)
	2.255 (2)			112.52 (6)
$(PPh_3)_2CuBr{\cdot}0.5C_6H_6$[b]	2.263 (2)	2.346 (2)	126.0 (1)	121.0 (1)
	2.282 (3)			112.8 (1)
$(PPh_2$-*o*-tol$)_2CuI$	2.255 (1)	2.507 (1)	126.36 (7)	116.82 (4)
$(PPh_3)_2CuI$[a]	2.273 (2)	2.524 (2)	126.9 (1)	116.61 (5)

[a] Reference 16. [b] Reference 17.

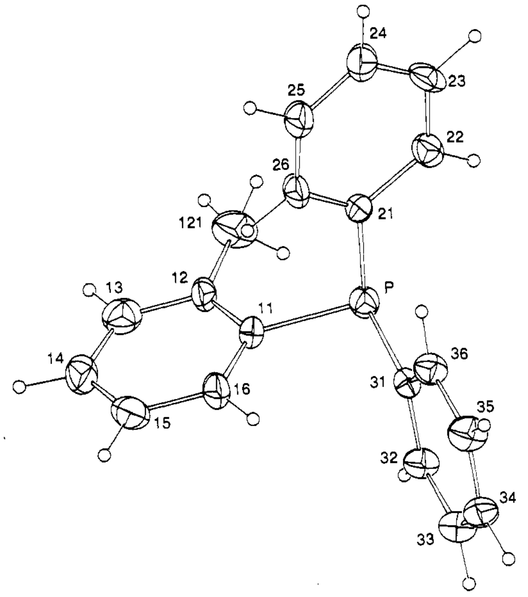


Figure 3. View of the molecule of PPh_2-*o*-tol. 20% thermal ellipsoids are shown in this and subsequent figures. Hydrogen atoms have an arbitrary radius of 0.1 Å.

87, 78, and 85°; $P(o\text{-tol})_3$ molecule 1, 84, 78, 86°; $P(o\text{-tol})_3$ molecule 2, 79, 89, and 86°. The consequent twisting of the phenyl rings about the P–C bonds, defined here by the angles between the normals to the base of the PC_3 pyramid and the planes of each phenyl group, are similar in PPh_3 and PPh_2-*o*-tol and range between 20 and 60°, with the twist about P–C always being in the same sense: PPh_3, 22, 54, and 25°; PPh_2-*o*-tol, 36, 26, and 47°. The almost C_3 symmetry adopted by both $P(o\text{-tol})_3$ molecules reflects the steric influence of the three tolyl groups on the conformational structure (molecule 1, 37, 49, and 43°; molecule 2, 55, 47, and 51°). In these molecules each ring is bent toward the lone pair with the angle P–C(1)–C(2) being 7–10° smaller than P–C(1)–C(6). For example with PPh_3, the P–C(1)–C(2) angles are 115.8 (4), 116.3 (4), and 116.2 (4)° and the P–C(1)–C(6) angles are 124.9 (4), 123.9 (4), and 123.2 (4)° while in the present structure these angles are 117 (1), 115 (1), and 116 (1)° and 123 (1), 125 (1), and 125 (1)°, respectively.

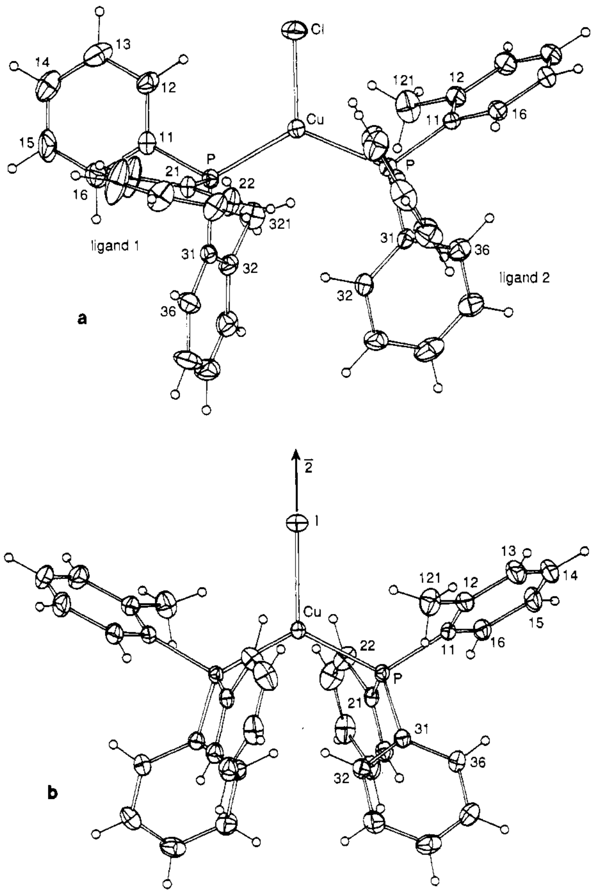
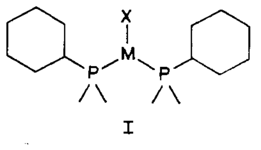


Figure 4. (a) Projection of $(PPh_2$-*o*-tol$)_2CuCl$ onto the P_2CuCl plane. (b) Projection of $(PPh_2$-*o*-tol$)_2CuI$ onto the P_2CuI plane.

In the $(PPh_2$-*o*-tol$)_2CuX$ complexes, the P–C distances are marginally shorter and the C–P–C angles slightly greater than the values found for the uncomplexed ligand: Cl, ⟨P–C⟩ = 1.820 (2) Å, ⟨C–P–C⟩ = 103.9 (2)°; Br, ⟨P–C⟩ = 1.816 (3) Å, ⟨C–P–C⟩ = 103.8 (4)°; I, ⟨P–C⟩ = 1.829 (2) Å, ⟨C–P–C⟩ = 103.9 (6)°. Complexation results in a significant diminution of the differences between P–C(1)–C(2) and P–C(1)–C(6) with the average difference in these angles for each of the three structures being 3.0, 3.3, and 3.7° respectively.

In the triphenylphosphine complexes $(PPh_3)_2CuX$, the phenyl groups of each ligand assumes the "W" conformation (I) in which



I

ring 1 of each ligand approaches coplanarity with the P_2CuX

plane, the conformational angle, X–Cu–P(*l*)–C(*l*11), ranging between 0 and 13° and the torsion angle of ring 1, Cu–P(*l*)–C(*l*1)–C(*l*12), varying between 17 and 39°. X···H(*l*12) contact distances are of the order of 2.7–2.9 Å.

The geometry of the P_2CuX core in these compounds was found to be unsymmetrical for the chloride and bromide, with differences of 5–9° in the X–Cu–P angles and small but consistent differences of 0.01–0.02 Å in the Cu–P distances, but symmetrical for the iodide, which crystallizes in a *C*2/*c* lattice with the Cu–I lying on a 2-fold axis of symmetry. In the present compounds, this conformational structure is not adopted. In both the chloride and bromide, each ligand adopts a skewed conformation with X–Cu–P(*l*)–C(*l*11) ranging from 26 to 33°, each ring being rotated to opposite sides of the P_2CuX plane (Table VII). For ligand 1, there are quite short X···H(112) contact distances (Cl, 2.7 Å; Br, 2.8 Å) for ring 1 and the Cu–P(1)–C(111)–(112) torsion angles are 20 and 23°, respectively, well within the range recorded for the analogous PPh_3 compounds, while the tolyl group is located in ring 3. For ligand 2, however, the tolyl group is found in ring 1, which in turn is twisted away from the halogen with torsion angles of 53 (Cl) and 54° (Br). In this conformation there are no methyl hydrogen–halogen contact distances less than 3.0 Å. In the iodide structure the tolyl group is located in ring 1 of the two symmetry-related ligands. As in ligand 2 of the chloride and bromide structures, this ring has a torsion angle greater than 50° with no short X···H contact distances. The angle I–Cu–P(1)–C(111) of 14° is, however, midway between the eclipsed and skewed conformations of $(PPh_3)_2CuX$ and $(PPh_2$-*o*-tol$)_2$CuCl,Br, respectively.

Consideration of the P_2CuX core geometries shows that the Cu–P distances in both the chloride and bromide are unsymmetrical (Cl, 2.241 (2) and 2.257 (2) Å; Br, 2.240 (2) and 2.255 (2) Å) and are ~0.02 Å shorter than the distances in the comparable PPh_3 complexes, as are the values for the iodide structure (2.255 (1) vs 2.273 (2) Å) (Table VIII). The variation in Cu–P distance with halide is even smaller than that found for the PPh_3 compounds. The P–Cu–P angles of 126.96 (7) and 127.89 (7)° for X = Cl and Br are ca. 2° greater than in the PPh_3 molecules, but this slight difference disappears for the iodide structures. In spite of the decrease in the Cu–P bond lengths, the Cu–X distances are also slightly shorter, the differences being 0.017 Å for the iodide structures, decreasing to 0.010 Å for the bromides and 0.003 Å for the chlorides, a possible influencing factor being changes in the influence of X···H interactions on the Cu–X bond length. The shorter Cu–I distance is consistent with the increased wavenumber observed for the Cu–I vibrational mode. The asymmetry in H···X interactions is reflected in the Cl,Br–Cu–P angles: Cl, 118.55 (7) and 113.61 (7)°; Br, 118.25 (6) and 112.52 (6)°.

Conclusions. Despite the significant conformational changes detailed above, the net effect on the core geometry of substituting a phenyl group of PPh_3 by an *o*-tolyl group is surprisingly small. Nevertheless, changes in the steric profile and X···H interactions caused by the introduction of this group into the ligand appears to result in a considerable simplification of the chemistry of adducts with CuX with three being the maximum coordination number of the copper atom attained. Preliminary X-ray results on reaction mixtures with 1:1 molar ratios of ligand to CuX show the crystalline products obtained to be the 1:1 dimeric species (PPh_2-*o*-tol)CuX_2Cu(PPh_2-*o*-tol).[26] As yet, we have no evidence for the formation of the 1.5:1 species commonly found for the PPh_3 system. Similarly, we have not been able to isolate 3:1 monomers by recrystallization from excess ligand. Examination of molecular models shows that situations in which the copper atom is four-coordinate, either in 3:1 monomers, 1.5:1 dimers, or 1:1 tetramers, results in considerable overlap of the methyl hydrogens with the other ligands. However, positive evidence for the existence or otherwise of four-coordinated copper species in this system must await a detailed solution equilibrium study similar to that recently reported for the PPh_3 and PPh_2Me systems.[27]

Acknowledgment. We acknowledge support of this work by a grant from the Australian Research Grants Scheme. The Bruker CXP-300 spectrometer is operated by the Brisbane NMR Centre, and we thank the Centre for making instrumental time available to us and Dr. Andrew Whittaker for recording the solid-state spectra. We thank Catherine Hobbis for capable assistance in the recording of the far-infrared spectra. Microanalyses were completed by the University of Queensland Microanalytical Service.

Registry No. (PPh_2-*o*-tol$)_2$CuCl, 110142-27-3; (PPh_2-*o*-tol$)_2$CuBr, 110142-28-4; (PPh_2-*o*-tol$)_2$CuI, 110142-29-5; Ph_2P-*o*-tol, 5931-53-3; Ph_2PCl, 1079-66-9; $CH_3C_6H_4MgCl$, 33872-80-9.

Supplementary Material Available: Tables Sup I–Sup XII, listing non-hydrogen thermal parameters, the derived hydrogen positions, and ligand non-hydrogen geometries (18 pages); tables of calculated and observed structure factors (39 pages). Ordering information is given on any current masthead page.

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