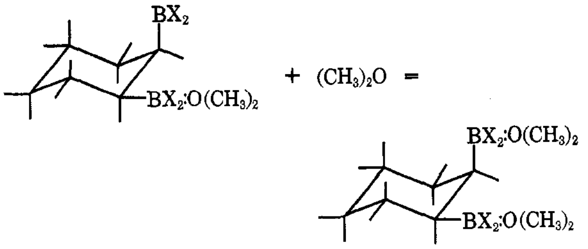
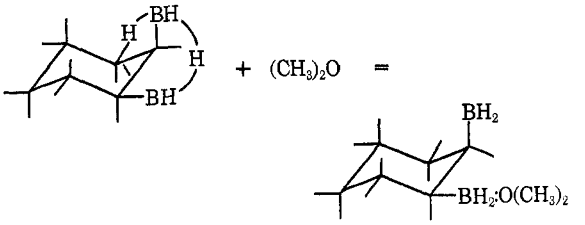


(3)

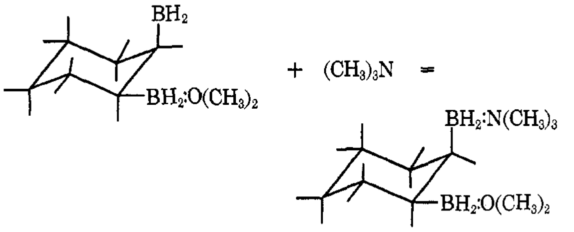
The relative degree of dissociation was indicated by the slope of the titration curves. It is seen that, for dimethyl ether, acid strength[11] is more important than steric requirements in determining the extent of donor–acceptor bond formation. With the bulkier Lewis base trimethylamine, an optimum balance of these two factors is achieved with II (Figure 3). The adducts of the more bulky acid I and the weaker acid IV are each more highly dissociated.

Quantitative displacement of coordinated ether can be effected by reaction of the adducts with the stronger amine base (Figure 4). In the titration curve, the first level portion and the inflection point showed formation of the 1:1 ether adduct



(4)

After the break, trimethylamine was added incrementally to the adduct solution. The second plateau indicated that the first mole equivalent of trimethylamine occupied the unused second acid site



(5)

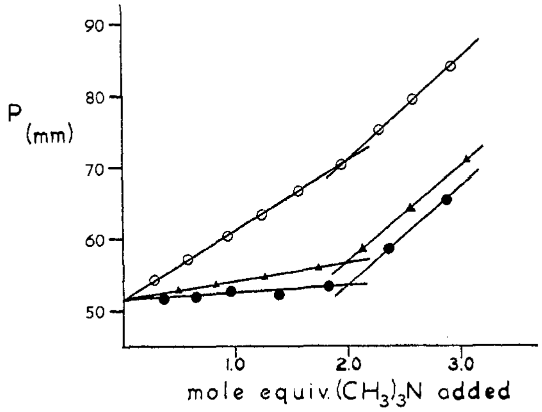


Figure 3.—Normalized tensimetric titration curve for reaction in hexane of *cis*-1,2-bis(dihaloboryl)cyclohexanes, $C_6H_{10}B_2X_4$, with $(CH_3)_3N$. Reaction temperature was 0°.

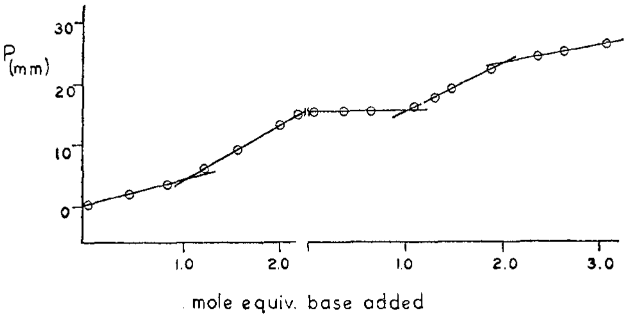
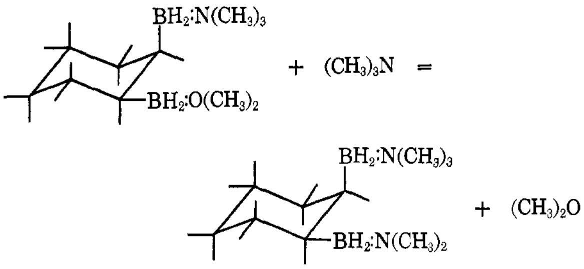


Figure 4.—Tensimetric titration curve for reaction in hexane of *cis*-1,2-bis(dihydridoboryl)cyclohexane, $C_6H_{10}B_2H_4$, with $(CH_3)_2O$ and subsequent displacement reaction with $(CH_3)_3N$. Reaction temperature was −45°.

The second rising portion of the curve occurred as the coordinated ether was displaced from the adduct



(6)

The last inflection point was observed as the formation of the 2:1 amine–acid adduct was completed.

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[11] P. H. Clippard and R. C. Taylor, *Inorg. Chem.*, **8**, 2802 (1969).

Correspondence

Factors Influencing the Stereochemistry of Four-Coordinate Copper(I)–Phosphine Complexes

Sir:

The structures of $((C_6H_5)_3P)_2CuX$ compounds, where X is a bidentate monoanion, were recently determined, primarily to elucidate the bonding between the X group and the copper atom.[1-4] A feature common to these complexes was the surprisingly large P–Cu–P angles, ranging from 120 to 131°. In order to evaluate plausible explanations[3,4] for the size and variation of the P–Cu–P angles and Cu–P bond lengths, a program of

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(1) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

(2) M. Bartlett and G. J. Palenik, *Acta Crystallogr., Sect. A*, **25**, S173 (1969).

(3) G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969).

(4) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969).

TABLE I

SUMMARY OF GEOMETRIC RESULTS FOR FOUR-COORDINATE COPPER(I)–PHOSPHINE COMPLEXES[a,b]

No.	Compd	Cu–P$_1$, Å	Cu–P$_2$, Å	Cu–X$_1$, Å	Cu–X$_2$, Å	P–Cu–P, deg	X–Cu–X, deg
1	$((C_6H_5)_3P)_2Cu(TFA)$[c]	2.258 (1)	2.256 (1)	2.096 (4)	2.077 (4)[d]	126.46 (5)	88.8 (1)
2	$((C_6H_5)_3P)_2Cu(TTA)$[c]	2.242 (2)	2.252 (1)	2.104 (4)	2.100 (4)[d]	127.53 (6)	88.7 (2)
3	$((C_6H_5)_3P)_2Cu(HFA)$[c]	2.239 (2)	2.236 (2)	2.123 (4)	2.117 (4)	127.10 (6)	86.6 (2)
4	$((C_6H_5)_3P)_2Cu(BH_4)$[e]	2.276 (1)[f]		2.02 (5)[f]		123.26 (6)	69.0 (3)
5	$((C_6H_5)_3P)_2Cu(B_3H_8)$[g]	2.274 (2)	2.288 (2)	1.84 (5)	1.85 (5)	119.97 (7)	103.0 (2)
6	$((C_6H_5)_2CH_3P)_2Cu(B_3H_8)$[h]	2.26 (1)	2.25 (1)	*i*	*i*	128 (1)	*i*
7	$((C_6H_5)_3P)_2Cu(NO_3)$[j]	2.256 (3)[f]		2.22 (1)[f]		131.2 (1)	57.5 (3)
8	$(Cy_3P)_2Cu(NO_3)$[k]	2.29 (1)		*i*	*i*	140 (1)	*i*
9	$((C_6H_5)_3P)_3Cu_2Cl_2 \cdot C_6H_6$[l]	2.25 (1)	2.27 (1)	2.44 (1)	2.47 (1)	130.4 (3)	91.6 (3)
10	$[((C_6H_5)_3P)_2CuN_3]_2$[m]	2.271 (4)	2.250 (3)	2.102 (10)	2.085 (10)	122.3 (1)	98.0 (4)
		2.269 (4)	2.266 (3)	2.109 (11)	2.116 (10)	120.8 (1)	99.7 (4)
11	$((C_6H_5)_2CH_3P)_3CuCl$[h]	(2.28, 2.30, 2.28)[n]		2.36		~115	~104[o]
12	$((C_6H_5)_3P)Cu(\pi\text{-}C_5H_5)$[p]	2.135 (1)		...	...	...	...

[a] Abbreviations: X, donor atom of the anion bonded to copper; Cy, cyclohexyl, TFA, trifluoroacetylacetonate ion; TTA, 2-thenoyltrifluoroacetonate ion; HFA, hexafluoroacetylacetonate ion. [b] Estimated standard deviations in the last figures are in parentheses. [c] M. W. Bartlett, Ph.D. Thesis, University of Waterloo, 1970. [d] Oxygen on the CF_3 side of the β-diketonate ring. [e] Reference 1. [f] Molecule has crystallographically required twofold symmetry axis. [g] Reference 4. [h] D. Stowens and D. A. Ucko, Columbia University, unpublished results. [i] Data not yet available. [j] Reference 3. [k] G. G. Messmer, University of Waterloo, unpublished results. [l] D.F. Lewis, S. J. Lippard, and P. S. Welcker, *J. Amer. Chem. Soc.*, **92**, 3805 (1970); the values quoted for this compound refer only to the tetracoordinate, not the trigonal, copper coordination geometry. [m] R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *ibid.*, **92**, 738 (1970). [n] Three phosphine groups. [o] Average P–Cu–Cl angles. [p] Reference 13.

X-ray structural studies, involving systematic variation of the tertiary phosphine ligand and the donor properties of the group X, was initiated.[5,6] A number of related copper(I)–phosphine complexes have also been characterized by X-ray diffraction in conjunction with investigations of the multiple equilibria occurring in solutions of these compounds,[7] for the role of steric factors in determining the position of such equilibria is becoming increasingly clear.[8] From the information gathered in these studies it has been possible to evaluate the factors influencing the stereochemistry of tetracoordinate cuprous–phosphine complexes, as discussed in the present report.

Results for a number of phosphine–copper(I) complexes are summarized in Table I. In compounds **1–3**, the R groups of the β-diketonate anion are varied whereas the pairs of compounds **5–6** and **7–8** have the same anion but different phosphine ligands. In two $((C_6H_5)_3P)_2CuX$ compounds, **9** and **10**, the anion X contains a second copper atom. Compounds **4**, **11**, and **12** are included for comparison purposes. The correlation between the average Cu–P distance and P–Cu–P angle for the eight $((C_6H_5)_3P)_2CuX$ complexes is shown in Figure 1.

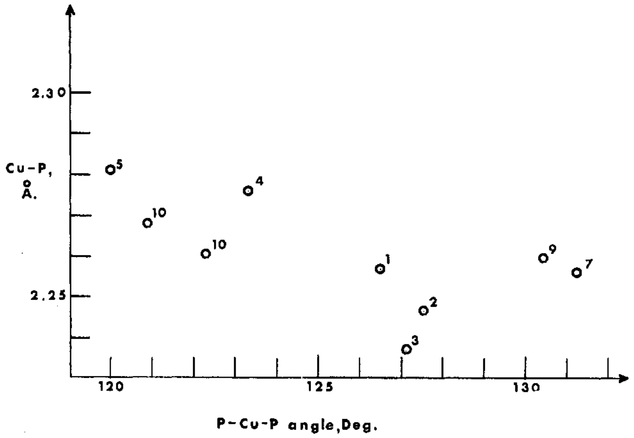

Figure 1.—Correlation of copper–phosphorus bond distances and interbond angles in $((C_6H_5)_3P)_2CuX$ complexes. For numbering scheme see Table I.

Several generalizations may be drawn from the data. These are first enumerated and then discussed in somewhat more detail in subsequent paragraphs. (1) The *increase* in P–Cu–P angles from the idealized value of 109.5° results primarily from stereochemical factors involved in packing ligands of unequal bulk around the spherical, d^{10} copper(I) atom. (2) *Trends* in P–Cu–P angles are best explained by consideration of steric effects across the P–Cu–X bonds. Within the series of $((C_6H_5)_3P)_2CuX$ molecules, the angles are largest for planar X ligands and decrease as the nonplanarity and general crowding of the X ligand increases. The "bite" distance of the X anion does not appear to be the dominant factor. (3) The inverse length and, by implication, the strength of the copper–phosphorus bonds correlate roughly with the per cent s-electron content in the bond, as judged by the size of the P–Cu–P angle. The sensitivity of metal–phosphorous bond lengths to their s-electron character has also been observed for phosphine complexes of other metals.[6] (4) For the homologous series of $((C_6H_5)_3P)_2CuX$ compounds with X being a β-diketonate anion (**1–3**), the Cu–P distances correlate with the donor strength of the X ligand, maintaining the charge balance on the copper atom. (5) The effect of copper–phosphorus π bonding is concluded to be minimal in determining trends in Cu–P distances.

The fact that P–M–P bond angles in pseudotetrahedral triphenylphosphine complexes can approach the idealized value has been established in numerous cases, including $((C_6H_5)_3P)_2NiBr_2$ [Ni–P = 2.333 (5) Å, P–Ni–P = 110.4 (2)°],[9] $((C_6H_5)_3P)_3Pt(CO)$ [Pt–P = 2.340 (8) Å, P–Pt–P = 111.4 (3)°],[10] and $((C_6H_5)_3P)_4RhH \cdot 0.5C_6H_6$ [Rh–P = 2.36 (3) Å, P–Rh–P = 109 (2)°].[11] For compounds **1–10**, the steric bulk of the

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(5) Recent work in Professor Mason's laboratory on third-row transition metal halide complexes with tertiary phosphine ligands has had similar, although not identical, objectives.[6]

(6) L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Commun.*, 30 (1970).

(7) (a) E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **92**, 4114 (1970); (b) S. J. Lippard and J. J. Mayerle, unpublished work.

(8) *Cf.*, for example, C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

(9) J. A. J. Jarvis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1473 (1968).

(10) V. G. Albano, G. M. B. Ricci, and P. L. Bellon, *Inorg. Chem.*, **8**, 2109 (1969).

(11) R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

ligand X is sufficiently small by comparison to the tertiary phosphine to permit expansion of the P–Cu–P angle. This effect is especially well illustrated by compound **8** which contains the very crowded tricyclohexylphosphine ligand; here the P–Cu–P angle opens to 140° (compare compound **7**). In compound **11** there are three phosphine ligands bonded to copper, which results in a reduction of the average P–Cu–P angle to $\sim$115°.

One of the more noteworthy features of the results summarized in Table I is the variation in P–Cu–P angle in $((C_6H_5)_3P)_2CuX$ compounds (**1**–**5**, **7**, **9**, **10**) with choice of anion. This trend can also be explained purely on steric grounds, and, while alternative explanations exist,[3,4] they involve complicating assumptions and will not be considered further. In particular, the largest angles occur in compounds where the X group is (to a first approximation) planar (NO_3^-, $Cl_2CuP(C_6H_5)_3^-$), and the smallest angles occur in compounds where the shortest Cu–X bonds are and where X is decidedly more bulky ($B_3H_8^-$, BH_4^-, and possibly the puckered azide dimer, **10**). Since the phenyl ring protons of the $(C_6H_5)_3P$ ligands extend well across the P–Cu–X angles,[1–4] the P–Cu–P angle can open only until there is a balance between nonbonded repulsions of $(C_6H_5)_3P$–$(C_6H_5)_3P$ and $(C_6H_5)_3P$–X types. Wherever possible there will be relief of intramolecular, interligand crowding, as illustrated by the rotation of the thienyl group in **2** so that the sulfur atom points away from the rest of the molecule and by the preference in the two $(C_6H_5)_2CH_3P$ complexes **6** and **11** for the rotational conformer which directs the methyl groups toward the anion. Comparison of the geometries for compounds **5** and **6** is especially revealing, where substitution of $(C_6H_5)_2CH_3P$ for $(C_6H_5)_3P$ reduces the steric interactions between phosphine and hydroborate groups with a resultant increase of 8° in the P–Cu–P angle.

As shown in Figure 1, there is a very approximate correlation among the P–Cu–P angles and Cu–P distances for the various $((C_6H_5)_3P)_2CuX$ compounds. The trend may be somewhat better than it appears from the figure, since no attempt has been made to correct for the widely variant electronic properties and chelate ring sizes of the anions, but there is clearly a need for more data. The increase in the per cent s character in the copper–phosphorus bonds with increasing angle results in shorter Cu–P distances, as would be expected from steric as well as theoretical considerations.[12] In the extreme case of $((C_6H_5)_3P)Cu(\pi\text{-}C_5H_5)$, the distance of 2.135 (1) Å is the shortest yet observed for a Cu–P bond, a result which has been attributed at least in part to steric factors.[13]

It is interesting to focus on the three β-diketonate complexes, **1**–**3**, where intramolecular steric interactions are nearly constant. The most electron donating of these ligands is trifluoroacetylacetonate, and compound **1** is observed to have the shortest Cu–O bond lengths. Correspondingly, the Cu–O bond lengths in the hexafluoroacetylacetonate complex, **3**, are longer. A parallel, but inverse, trend occurs in the Cu–P bond distances for these three compounds indicating that, as the donor strength of the anion varies, an adjustment occurs in the copper–phosphorus σ bonding in order to maintain a balance of total charge density contributed by the ligands to the copper atom.[14–16] It may be noted (Table I) that the P–Cu–P angles follow nearly the same trend, with the greater steric relief of the TTA ligand (the thienyl group is planar and almost coplanar with the β-diketonate backbone) allowing the P–Cu–P angle to open a little more. It is also of interest that, since the donor strengths of the β-diketonate ligands correlate with the Cu–P bond lengths, copper–phosphorus back (π)-bonding appears to be minimal. If π bonding were operative, the Cu–P distances would be expected to decrease as negative charge accumulated on the copper atom.

Although the foregoing discussion has been specifically limited to copper(I) complexes with tertiary phosphine ligands, the conclusions are considered to be more generally applicable, especially to four-coordinate d^{10} systems where substantial metal–ligand π bonding is absent. For example, it would appear that structural results for certain Zn(II) complexes containing nitrogen and chloride donor ligands[17] could be explained in an analogous manner, although extensive data are not available.[18,19] The appearance of new structural results which should be "predictable" by inductive reasoning from the five generalizations will be of interest.

Acknowledgments.—We are grateful to the National Science Foundation (S. J. L.) and the National Research Council of Canada (G. J. P.) for their support of this work and to our postdoctoral and student collaborators, cited in the individual references, for their assistance. S. J. L. also wishes to thank Professor G. M. Whitesides for his valuable comments and the Alfred P. Sloan Foundation for a research fellowship, 1968–1970.

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[12] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[13] F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **92**, 2353 (1970).

[14] The inductive effect of the β-diketonate anion alters the net positive formal charge on the copper atom resulting in weaker (longer) or stronger (shorter) Cu–P bonds. The concept of ligand inductive effects has been introduced by previous investigators, for example, in the interpretation of electronic[15] or infrared[16] spectral results.

[15] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).

[16] W. A. G. Graham, *ibid.*, **7**, 315 (1968), and references cited therein.

[17] H. S. Preston and C. H. L. Kennard, *J. Chem. Soc. A*, 1956 (1969).

[18] In at least one instance,[19] the existence of interligand nonbonded interactions has actually been cited in partial support of the formulation of a species, the $Ir(NO)_2(P(C_6H_5)_3)_2^+$ cation, as a tetrahedral d^{10} rather than a planar d^8 complex, since planar d^8 compounds generally show only small distortions due to intramolecular steric factors.

[19] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).

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RECEIVED SEPTEMBER 22, 1970

Reevaluation of the Dipolar Contribution to the Contact Shifts of the Square-Planar Complex Bis(dithioacetylacetonato)cobalt(II)

Sir:

Recently,[1] we have interpreted the nmr contact shift data for the square-planar complex $Co(SacSac)_2$

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[1] R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, **8**, 2265 (1969).