cally destabilized dianion rotomer (**43c** $\rightleftarrows$ **43t**) to produce trianion **44c** or **44t** which, in turn, decomposes to dienolate **45c** or **45t**, respectively. Geometrical equilibration at the trianion stage (**44c** $\rightleftarrows$ **44t**) is an additional rationale which makes parallel stereochemical predictions for this trianion reaction.[18]

The product stereochemistry seems to be primarily determined by minimization of steric interactions in intermediates **43** or **44.** In the case where $R^1 = H$ (**12**), the R^2 group apparently prefers to be orientated away from lithiosulfonamide group resulting in formation of cis olefin **24.** When R^1 is an alkyl group (**10, 11**), the situation appears more balanced and a cis–trans mixture of olefins is formed (**21a,b, 22a,b**). Where R^1R^2 are part of a large ring (**18**), the cis orientation (**43c** or **44c**) is further destabilized by additional interactions between the ring methylenes and the alkoxy group of the ester. This cumulative effect presumably overcompensates for the R^2-sulfonamide interaction which, in turn, results in the formation of trans olefin (**30**). This latter effect is consistent with the observed shift toward trans olefin in the acyclic case where an additional methylene group was added to the R^1 and R^2 moieties (c.f. **10** vs. **11**).[19]

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(16) We are actively engaged in pursuing experimental modifications designed to allow sequential bis functionalization of these dilithio species.

(17) Trapping off the vinyl anion intermediate, **5**, in the Shapiro reaction is not achieved unless TMEDA is used as the solvent.[2]

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(21) Alfred P. Sloan Fellow 1977–1979.

C. A. Bunnell,[20] P. L. Fuchs*[21]
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Nickel Phosphine Complexes. Crystal and Molecular Structure of a New Nickel(I) Complex: $[Ni(P(CH_3)_3)_4]B(C_6H_5)_4$

Sir:

The interest in Ni(II) phosphine complexes has increased considerably in recent years because of their values as promoters in organic syntheses such as cross-coupling reactions,[1,2] carbonylation,[3] cyclotrimerization of ethylene,[4] .... In these reactions, the formation, the stereochemistry, and the oxidation–reduction equilibria of alkylphosphine–nickel complexes are of great importance since they are central to the understanding of the catalytic cycle. On the basis of the 16 and 18 electron rule, it has been assumed[5] that these reactions imply diamagnetic Ni(II) d^8 or Ni(0) d^{10} complexes as active intermediates. Paramagnetic d^9 species (17 electron complexes) have not usually been considered.

Recently, Klein et al.[6] have reported the synthesis of new pentacoordinate $[Ni(CH_3)(P(CH_3)_3)_4]^+X^-$ complexes. Since very few pentacoordinate $[NiXL_4]^+$ compounds have been reported, we planned to determine the x-ray structure of the $[Ni(CH_3)(P(CH_3)_3)_4]BPh_4$ complex. Orange red crystals were obtained by crystallization from a solution of the five-coordinate complex in tetrahydrofuran. It turns out, surprisingly after the crystal structure analysis, that a dissociative reduction of the $[Ni(CH_3)(P(CH_3)_3)_4]BPh_4$ species occurs and that the isolated complex is the unexpected nickel(I) $[Ni(P(CH_3)_3)_4]BPh_4$ compound.[7] We report here the crystal and molecular structure of this Ni(I) complex.

It crystallizes in the monoclinic space group $P2_1/c$ with four units per cell ($\rho_m = 1.145$ (5) g/cm^3) of dimensions $a = 16.153$ (3) Å, $b = 12.540$ (2) Å, $c = 20.880$ (3) Å, $\beta = 111.54$ (2)°. Intensity data were collected from a single crystal sealed in a Lindemann glass capillary mounted on an automatic diffractometer (Enraf-Nonius, CAD-4) using Mo Kα radiation. The structure was solved from Patterson and Fourier synthesis and

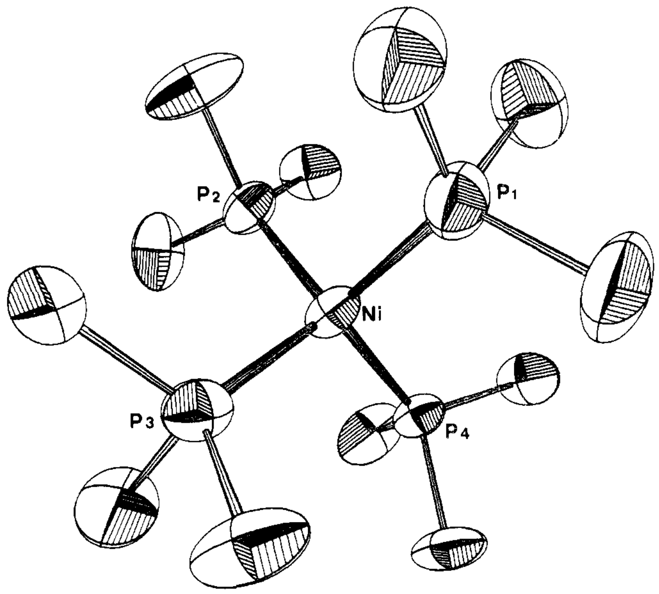

Figure 1. Perspective view of the $[Ni(P(CH_3)_3)_4]^+$ cation.

Table 1. Selected Interatomic Distances (Å) and Bond Angles (Degrees) for the $Ni[(P(CH_3)_3)_4]^+$ Cation

Bond	Å	Angle	Degree
Ni-P(1)	2.213 (3)	P(1)-Ni-P(2)	106.0 (1)
Ni-P(2)	2.211 (3)	P(1)-Ni-P(3)	104.6 (1)
Ni-P(3)	2.221 (3)	P(1)-Ni-P(4)	108.0 (1)
Ni-P(4)	2.221 (3)	P(2)-Ni-P(3)	106.1 (1)
		P(2)-Ni-P(4)	119.9 (1)
		P(3)-Ni-P(4)	111.0 (1)

refined by full matrix least-squares techniques using 2008 independent reflections above background. In the refinement, the phenyl groups were treated as rigid bodies, the Ni, P, B, and methyl C atoms were assigned anisotropic thermal parameters. The final R index was 0.054 (R_W = 0.048) for 215 variables.[8] The last difference Fourier map showed no peak higher than 12% of the mean height of a C atom on a Fourier map.

The structure consists of discrete, well-separated $[Ni(P(CH_3)_3)_4]^+$ cations (Table I) and $[B(C_6H_5)_4]^-$ anions (Figure 1). No extra methyl group can be located either at the nickel atom or at any other place in the cell. The coordination geometry of Ni can be described in terms of a slightly distorted tetrahedron. The main bond distances agree well with the literature values, and are in the range reported for Ni(II) phosphine complexes.[9] The phenyl rings in $[B(C_6H_5)_4]^-$ show no unexpected features and the shortest Ni-C (phenyl) and Ni-H (phenyl) distances are 5.58 and 5.25 Å, respectively, excluding any phenyl-Ni interaction.

Since the crystallographic evidence indicates that the compound is a monomeric Ni(I) tetrahedral complex, and since very few such complexes have been reported,[10] we record here some of its physical properties.

The measured specific mass of a single crystal, 1.145 (5) g/cm^3, is in better agreement with the theoretical value, 1.152 (2) g/cm^3, calculated for $[Ni(P(CH_3)_3)_4]B(C_6H_5)_4$ than with 1.177 (2) g/cm^3 calculated for $[Ni(CH_3)(P(CH_3)_3)_4]B(C_6H_5)_4$.

The magnetic moment measured at room temperature, μ_{eff} = 2.40 μ_B, confirms the presence of one unpaired electron. This value is higher than the one generally reported for tetrahedral d^9 complexes (1.93-1.98 μ_B) which are generally distorted, but remains near the value of 2.2 μ_B calculated for undistorted tetrahedral d^9 complexes.[11]

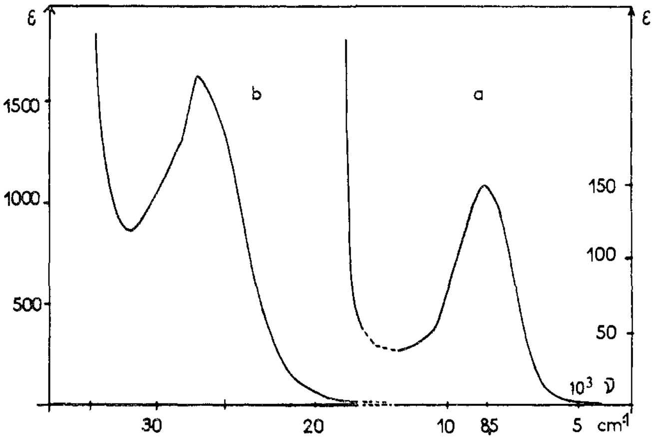

Figure 2. Room temperature electronic spectrum of $[Ni(P(CH_3)_3)_4]B(C_6H_5)_4$ in CH_2Cl_2 solution (PMe_3 in excess): (a) ligand field spectrum; (b) charge-transfer spectrum.

The existence of $[Ni(P(CH_3)_3)_4]B(C_6H_5)_4$ in solution is confirmed by ESR and variable-temperature electronic spectroscopy. The ESR spectrum, at 77 K in CH_2Cl_2, exhibits a weak, broad, isotropic signal, from which an isotropic $\langle g \rangle$ value of 2.12 is calculated, in good agreement with the $\langle g \rangle$ value of 2.123 reported for the tetrahedral bis(cyclooctadiene-1,5)nickel(I) complex.[12] The electronic spectrum is shown in Figure 2. It presents the features expected for an undistorted tetrahedral d^9 complex, i.e., a single ligand field band at 8500 cm^{-1} (ϵ >150) ($^2T_2 \rightarrow {}^2E$). Another band, with two shoulders (24 000 and 29 500 cm^{-1}) is resolved at 26700 cm^{-1} and can reasonably be attributed to charge-transfer transitions. Even when prepared in an inert atmosphere, dilute solutions become rapidly opalescent owing to dissociation of the complex. This dissociation is limited by the addition of an excess of the phosphine ligand.

In addition to being the first accurate x-ray structure determination of a tetrahedral Ni(I) complex containing four monodentate identical ligands, this result shows, unambiguously, for the first time, that a reductive elimination to give a 17 electron paramagnetic species can occur in alkylnickel(II) phosphine systems. Thus, the reported catalytic mechanisms involving Nickel have to be carefully considered owing to the possible existence of highly reactive paramagnetic species. Further investigations on this problem are in progress.

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A. Gleizes, M. Dartiguenave,* Y. Dartiguenave, J. Galy
Laboratoire de Chimie de Coordination du CNRS
BP 4142, 31030 Toulouse Cedex, France

H. F. Klein
Anorganisch-Chemisches Institut der Technischen Universität
München, Arcisstr. 21, D-8000 Munchen 2, West Germany

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Structural Implications for Blue Protein Copper Centers from Electron Spin Resonance Spectra of $Cu^{II}S_4$ Chromophores[1]

Sir:

Current interest in copper(II)-sulfur bonding has been stimulated by the finding of the copper(II)-sulfur (cysteine) bond being involved in the copper centers in "blue" copper proteins.[2] It has recently been shown[3-5] that the intense blue coloration and high positive redox potentials in these proteins can be mimicked by simple inorganic compounds containing copper(II)-sulfur bonding. However, the origin of the anomalously small hyperfine (hf) coupling constants in the electron spin resonance (ESR) spectra of "blue" proteins is as yet uncertain.[6,7] Several compounds containing copper(II)-sulfur bond(s) have been proposed as models for the "blue" copper centers, but they all show too large $|A_\parallel|$ and/or $g_\parallel$ values.[8-10] Thus, the proposed spatial disposition of ligand atoms around the "blue" copper centers varies from flattened tetrahedral,[11] trigonal-bipyramidal,[12] and pentacoordinated[13] to planar.[3,4] The diversity of these models appears to result mainly from the paucity of pertinent ESR data, especially for tetrahedral copper(II) centers containing copper(II)-sulfur bonding.

We wish to report here preliminary results from single-crystal ESR measurements for a tetrahedral $Cu^{II}S_4$ center, in comparison with the ESR data for an appropriate square planar $Cu^{II}S_4$ center in a frozen glass. The tetrahedral $Cu^{II}S_4$ centers were produced by ^{60}Co γ-irradiation of a single crystal of tetrakis(thioacetamide)copper(I) chloride, a technique originally used for generation of copper(II) sites in a copper(I) lattice in the case of $Cu(CH_3CN)_4^{2+}$.[9] All experiments were performed at liquid nitrogen temperature. The generation of two copper(II) species was observed; the angular variation of the g values of the dominant species is depicted in Figure 1. If an irradiated crystal was allowed to warm to near-ambient temperature, the resonances attributable to cupric centers disappeared, as has been observed previously for a tetrahedrally distorted $Cu^{II}S_4$ species.[10]

Our preliminary result shows that (i) the ESR spectra of the major $Cu^{II}S_4$ center produced by γ-irradiation can be described by $g_x = g_y = 2.027$, $g_z = 2.152$, $|A_x| = |A_y| = 24$, $|A_z| = 86.9 \times 10^{-4}$ cm^{-1}, (ii) the principal axes of the g and A tensors coincide with each other, and (iii) the z axis is parallel to the crystallographic c axis. In this tetragonal crystal the copper(I) ion is surrounded almost tetrahedrally by four sulfur atoms in S_4 symmetry, and the dihedral angle between CuS_2 planes is 84.2°.[14] The crystal c axis is the direction of compression (flattening) of the CuS_4 tetrahedra. Since (i) the lowest field lines show splitting characteristic of the isotopes ^{63}Cu and ^{65}Cu, (ii) no ligand superhyperfine structure was observed, (iii) the principal g and A values are both small, which is expected for sulfur coordination,[7] (iv) the symmetry of the g and A tensors is as high as the crystal symmetry, and (v) the $g_\parallel$, $|A_\parallel|$ data lie in the $|A_\parallel|$, $g_\parallel$ region defined by the other CuS_4 centers (vide infra), these paramagnetic centers are certainly due to tetrahedral $Cu^{II}S_4$ chromophores.

Table I. Comparison of ESR Data of Copper Compounds Containing CuS_4 or Tetrahedral Coordination

Compd[a]	Core	Geometry[b]	$g_\parallel$	$\lvert A_\parallel\rvert$ (10^{-4} cm^{-1})	Ref
$[Cu(S{=}C(CH_3)NH_2)_4]^{2+}$	CuS_4	t	2.152	86.9	*c*
Cu^{2+} in tmtd	CuS_4	t?	2.1253	91.9	*d*
$Cu(SPh_2PNPPh_2S)_2$	CuS_4	?	2.107	119	*e*
$(Cu{:}Zn)(S_2CNEt_2)_2$	CuS_4	p	2.107	143	*f*
$[Cu(TTP)]^{2+}$	CuS_4	p	2.086	147	*c*
$[Cu{:}Ni(TTP)]BF_4$	CuS_4	p	2.087	172	*g*
$(Cu{:}Ni)(S_2P(OEt)_2)_2$	CuS_4	p	2.0855	150.6	*h*
$[(Cu{:}Ni)(i\text{-}mnt)_2]^{2-}$	CuS_4	p	2.086	156.0	*h*
$(Cu{:}Ni)(S_2CNEt_2)_2$	CuS_4	p	2.0856	156.2	*h*
$[(Cu{:}Ni)(mnt)_2]^{2-}$	CuS_4	p	2.0837	160.5	*h*
$[(Cu{:}Ni)(S_2C_2O_2)_2]^{2-}$	CuS_4	p	2.0805	163.9	*h*
$[Cu(FDT)_2]^{2-}$	CuS_4	p?	2.094	177.1	*i*
$[Cu(NCCH_3)_4]^{2+}$	CuN_4	t?	~2.32	~80	*j*
$[Cu(NCS)_4]^{2-}$	CuN_4	t	~2.43	89	*k*

[a] Abbreviations: tmtd, tetramethylthiouram disulfide; i-mnt, 1,1-dicyano-2,2-dithioethylene; mnt, 1,2-dicyano-1,2-dithioethylene; FDT, fulvenedithiolate; TTP, 1,4,8,11-tetrathiacyclotetradecane. [b] t, tetrahedral; p, planar. [c] This work: the minor component has $|A_\parallel| = 69.4 \times 10^{-4}$ cm^{-1}, $g_\parallel = 2.080$. [d] Reference 19. [e] Reference 10. [f] M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, **7**, 2548 (1968). [g] L. K. White and R. L. Belford, *J. Am. Chem. Soc.*, **98**, 4428 (1976). [h] B. Malmström, B. Reinhammer, and T. Vänngård, *Biochim. Biophys. Acta*, **156**, 67 (1968); **205**, 48 (1970). J. Peisach, W. G. Levine, and W. E. Blumberg, *J. Biol. Chem.*, **242**, 2847 (1967). [i] P. C. Savino and R. D. Bereman, *Inorg. Chem.*, **12**, 173 (1973). [j] Reference 9. [k] K. D. Forster and V. Weiss, *J. Phys. Chem.*, **72**, 2669 (1968).

Both perchlorate and tetrafluoroborate salts of the planar macrocycle[3,4] $Cu(TTP)^{2+}$ gave essentially the same ESR spectrum, characterized by small $g_\parallel$ and moderately large $|A_\parallel|$ values, in line with other planar $Cu^{II}S_4$ moieties (TTP, 1,4,8,11-tetrathiacyclotetradecane).

Table I summarizes all the available ESR data for $Cu^{II}S_4$ and tetrahedrally coordinated copper(II) centers, with biologically reasonable donor atoms. An examination of Table I, coupled with the data for planar or distorted octahedral compounds,[15] reveals the following salient features: (i) all of the $Cu^{II}S_4$ centers show small $g_\parallel$ values, ~2.09 to ~2.15, (ii) the (flattened) tetrahedral coordination produces small $|A_\parallel|$ values, which are half or less than half of those for planar or distorted octahedral centers,[15] (iii) as for CuN_4 centers,[16] the $g_\parallel$ values of the CuS_4 loci decrease as $|A_\parallel|$ increases (Figure 2, a schema of the $|A_\parallel|$ vs. $g_\parallel$ values for CuS_4 and CuN_4 centers, reiterates the correlation[7,10,16] between these parameters for a given set of donor atoms and shows an almost linear relationship between them).

Peisach and Blumberg[7] have shown that positive charge on a five-atom CuX_4 core can reduce $|A_\parallel|$ and increase $g_\parallel$. The effect is greater for CuS_4 than for CuN_4 centers,[7] but is less influential for nitrogen-bonded copper than is the now well-established effect of tetrahedral distortion on planar CuN_4 moieties,[16] which is also to decrease $|A_\parallel|$ and increase $g_\parallel$.

The ESR results for $Cu(TTP)^{2+}$ suggest that the charge factor alone cannot reduce $|A_\parallel|$ to the level observed for blue protein copper. Comparison of our data with that of Davis et al.,[17] for $Cu(TTP)^{2+}$ in the Ni-complex lattice as a planar CuS_4 unit with one weakly interacting BF_4^-, shows in addition that the effect of axial (ligand) perturbation of the CuS_4 square is to reduce $|A_\parallel|$ by only 15%, as expected.[18] We therefore propose that the above data enable a choice to be made in favor