gave as the predominant product 2-penten-1-ol (**12**), demonstrating that conjugate addition is the preferred mode of reaction. The reaction was stereoselective for the trans alcohol **12**, not only for lithium dimethylcuprate but for all the other reagents as well.[11,12]

[11] Stereoselectivity for the trans olefin is also observed for the reaction of lithium dialkylcuprates with allylic acetates; see ref 7b.

[12] After the completion of the study described in this paper we learned of the complementary work by R. J. Anderson discussed in the accompanying communication (*J. Amer. Chem. Soc.*, **92**, 4978 (1970)). We thank Mr. Anderson for discussions prior to publication.

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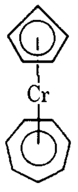
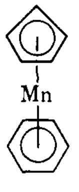
Formation and Structure of a New Mixed Sandwich Complex, $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3Ph_3)$

Sir:

The effective atomic number rule suggests that, among first-period transition metals, a series of mixed sandwich complexes might be expected, in which a π-cyclopentadienylmetal moiety interacts with carbocyclic ring systems of varying sizes,[1] *viz.*



1



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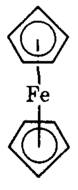

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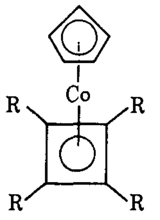
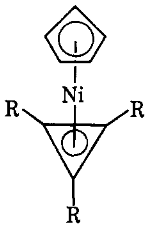


4, R = H
5, R = Ph



6, R = H
7, R = Ph

Compounds **1** through **5** are presently known,[2–7] and we now report the first authenticated[8] example in this isoelectronic series in which a nickel atom is symmetrically bonded to both five-membered and three-membered unsaturated carbocyclic rings.

π-Cyclopentadienyl-π-triphenylcyclopropenylnickel, **7**, has been obtained in 78% yield from a reaction between $[(\pi\text{-}C_3Ph_3)NiBr(py)_2]\cdot py$[9] and cyclopentadienylthallium in benzene solution at room temperature. After filtration (preferably under nitrogen) of thallium bromide and evaporation of the solvent *in vacuo*, the product was recrystallized from heptane to afford air-stable crystals, mp 137–138°. *Anal.* Calcd for $C_{26}H_{20}Ni$: C, 79.84; H, 5.15; mol wt, 390. Found: C, 79.64; H, 5.05; mol wt, 390 (mass spectrometry), 386 (osmometry in benzene). The proton nmr spectrum of the new complex in deuteriochloroform solution consists of a sharp singlet at τ 4.72, assignable to protons of the $\pi\text{-}C_5H_5$ group, and multiplet absorption due to protons of the phenyl substituents centered at τ 2.47. The mass spectrum of **7** exhibits, among others, prominent peaks at *m/e* 390 (molecular ion), 267 $(C_3Ph_3)^+$, and 123 $(C_5H_5Ni)^+$. The transition 390 → 267 + 123 is supported by a metastable peak at 182.8.

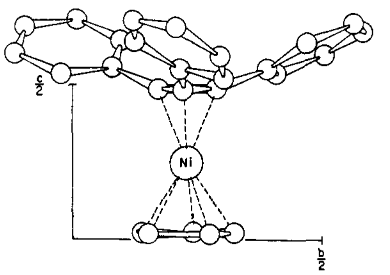


Figure 1. A molecule of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}Ph_3C_3)$ as viewed along the crystallographic *a* axis.

This nickel complex, **7**, crystallizes as deep red-orange prisms in the orthorhombic space group $Pna2_1$, $a = 21.003\ (1)$, $b = 12.360\ (1)$, $c = 7.496\ (1)$ Å, $Z = 4$. Intensity data were collected on a GE XRD-5 diffractometer by the moving-crystal, moving-counter method using Cu Kα radiation. The structure was solved by the usual heavy-atom techniques and has been refined to a conventional *R* factor of 0.062.

The structure shows that the nickel atom is complexed in a true sandwich fashion between the parallel cyclopentadienyl and triphenylcyclopropenyl rings (Figure 1). The nickel–cyclopropenyl carbon distances are identical within experimental error and average 1.961 (3) Å, while the nickel–cyclopentadienyl carbon distances average 2.11 (1) Å. As expected, the carbon–carbon distances within the cyclopropenyl ring (average = 1.432 (5) Å) are longer than those found in the free ligand, $(C_3Ph_3)(ClO_4)$[10] (average = 1.373 (5) Å), but are essentially equal to those found in $[(\pi\text{-}C_3Ph_3)NiCl(py)_2]\cdot py$,[11] average = 1.422 (8) Å. The three phenyl rings of the triphenylcyclopropenyl group are both tilted out of the plane of the cyclopropenyl ring away from the nickel atom and rotated about their respective axes by 20 (1)° to produce a "propeller" configuration. This effect, attributable to some combination of steric and hybridization factors, has been found in other similar complexes.[11,12] The cyclopentadienyl carbon–carbon distances average 1.41 (2) Å, although this ring suffers some rotational disorder in the crystal.

Bonding in this nickel sandwich compound can probably best be visualized in terms of the following two major contributions: (1) overlap of the a_1 combination of pπ atomic orbitals (C_{3v} localized symmetry) on the

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[1] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

[2] *Cf.* M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 190.

[3] R. G. Amiet and R. Pettit, *J. Amer. Chem. Soc.*, **90**, 1059 (1968).

[4] M. Rosenblum and B. North, *ibid.*, **90**, 1060 (1968).

[5] A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **34**, 452 (1961).

[6] M. D. Rausch and R. A. Genetti, *J. Amer. Chem. Soc.*, **89**, 5505 (1967).

[7] Compound **6** is presently unknown, although the cyclopropenium cation has been synthesized: R. Breslow, J. T. Groves, and G. Ryan, *ibid.*, **89**, 5048 (1967).

[8] Complex **7** was briefly mentioned in an earlier publication, but no details were given [R. G. Hayter, *J. Organometal. Chem.*, **13**, P1 (1968)].

[9] E. W. Gowling, Ph.D. Thesis, Sheffield University, 1965.

[10] M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

[11] D. L. Weaver and R. M. Tuggle, *ibid.*, **91**, 6506 (1969).

[12] R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, **18**, 614 (1965).

cyclopropenyl ring with a suitable nickel hybrid orbital (d_{z^2}, s and p_z contribution) and (2) interaction of the a_1 and e_1 combinations (C_{5v} localized symmetry) of the pπ orbitals on the cyclopentadienyl ring with an a_1 and e_1 set on the nickel atom.

Nickel complex **7**, like the isoelectronic cobalt analog **5**,[6] might be expected to undergo various aromatic-type ring substitution reactions, and studies along these lines are currently in progress.

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Triplet Ground State in the Dimer Bis(pyridine *N*-oxide)copper(II) Nitrate

Sir:

While there are great numbers of dimeric copper(II) complexes which exhibit low magnetic moments as a result of electronic spin–spin coupling giving singlet ground states,[1] there have been, up to now, no well-documented examples of copper dimers with triplet ground states. There are at least two reasons for the absence of examples of copper(II) dimers with triplet ground states. First, owing to the irregularities in the structure of copper(II) complexes, few adjacent copper ions have their unpaired electrons in orthogonal interacting orbitals as required for triplet ground states. The negative terms in the expression for the exchange coupling constant, J, are weighted by the overlap integral, S, and will disappear when the overlap integral is zero. The remaining positive term is not multiplied by S.[2] In addition to the potentially fewer numbers of copper dimers with $+J$, the probability of finding examples is diminished by the experimental difficulties which are present. First, copper complexes with "normal" moments do not attract much attention, and consequently crystallographers have not provided much structural information on dimeric copper complexes with "normal" moments. Secondly, only low-temperature magnetic susceptibility measurements and electron paramagnetic resonance experiments will provide the necessary documentation.

We have been systematically searching for copper dimers with triplet ground states and present electron spin resonance and static magnetic susceptibility data here which indicate that the electronic spin–spin interaction in the dimeric molecule bis(pyridine *N*-oxide)copper(II) nitrate yields a triplet ground state. The crystal structure of $[Cu(C_5H_5NO)_2(NO_3)_2]_2$, schematically shown in Figure 1, has been determined by Šćarničar and Matković.[3] Each copper ion is in a tetragonal pyramidal environment with trans pyridine *N*-oxide molecules and nitrate groups in the plane of the pyramid, and with an oxygen from a pyridine *N*-oxide in the plane of the neighboring copper ion occupying the fifth coordination position at the apex of the pyramid.

We have measured the magnetic susceptibility of a sample[4] of this compound in the range 2.4–300°K with a Foner-type[5] vibrating sample magnetometer[6] and a Faraday balance.[7] The data obey the Curie–Weiss law with a value for C of 0.449 emu deg mol^{-1}, which yields a magnetic moment of 1.90 BM per copper(II) ion. The intercept of the temperature axis at $\chi^{-1} = 0$ is $+2$°K. The magnetic data can be described in terms of the Van Vleck equation (1) for exchange-coupled pairs of copper ions with $J \sim 15$ cm^{-1} and $\langle g \rangle = 2.11$. Unfortunately, the calculated

$$\chi_m = \frac{g^2N\beta^2}{3kT}\{1 + {}^1/_3 \exp(-2J/kT)\}^{-1} \qquad (1)$$

susceptibilities are not very sensitive to the choice of J, but the value obtained here is in good agreement with that estimated from the electron spin resonance data given below. The discrepancy between observed and calculated susceptibilities for small negative values of J was markedly greater than that of the assigned value of J.

The epr spectrum at 300° of a powdered sample of $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ yields one broad line centered at 3100 G. At 77° additional lines, one at 3067 G and a less intense line at $\sim$1500 G due to the $\Delta M_s = \pm 2$ transition,[8] can be resolved. There is no further change in the spectrum at 4.2°K. However, the epr spectrum of a magnetically dilute sample prepared by substituting zinc ions for copper[9] provides the most convincing evidence for the triplet state. The sample was prepared by mixing 2,2-dimethoxypropane solutions of copper(II) nitrate and zinc nitrate in the molar ratio of 1:9 and the stoichiometric amount of pyridine *N*-oxide. At 77°K a powdered sample gives an epr spectrum with a very intense absorption near 3050 G on which the expected copper hyperfine structure is seen. On the low-field side, the separation between these components is 90 G. This absorption arises from copper ions in spin state $S = {}^1/_2$ which are present in dimeric molecules with neighboring zinc ions, *i.e.*, in $[Zn(Cu)(C_5H_5NO)_4(NO_3)_4]$. In addition to the intense absorption at 3050 G, as shown in Figure 2,

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(1) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 64, 99 (1964).

(2) R. L. Martin, "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N. Y., 1968.

(3) S. Šćarničar and B. Matković, *Chem. Commun.*, 297 (1967); *Acta Crystallogr., Sect. B*, 25, 2046 (1969).

(4) *Anal.* Calcd for $Cu(C_5H_5NO)_2(NO_3)_2$: C, 31.80; H, 2.67; N, 14.83. Found: C, 31.79; H, 2.71; N, 14.85.

(5) S. Foner, *Rev. Sci. Instrum.*, 30, 548 (1959).

(6) E. R. Jones, Jr., O. B. Morton, L. Cathey, T. Auel, and E. L. Amma, *J. Chem. Phys.*, 50, 4755 (1969).

(7) W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, 5, 1855 (1966).

(8) All line positions have been adjusted to be correct for a frequency of 9.182 GHz.

(9) The X-ray powder patterns of $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ and the solid solution are nearly identical. *Anal.* Found for $[Cu(Zn)(C_5H_5NO)_2(NO_3)_2]_2$: C, 31.95; H, 2.61; N, 14.80.