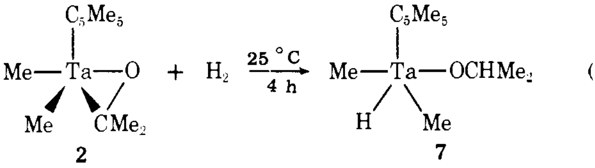
described as an oxycarbene ligand[3] which couples to a methyl (in **5**) or acetone carbon atom (in **4**) to give **6**, which then rearranges to **3**. If **4** is an intermediate, the coupling reaction must be rather specific and $Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-acetone})_2$ cannot form reversibly to any significant extent.

The course of the reaction of **2** with H_2 may prove relevant to the question of whether **4** or **5** is formed. At 25 °C in benzene under 40 psi of H_2, **2** smoothly and quantitatively is converted into **7** in 4 h (eq 3).[17] The fact that no methane is formed



(3)

suggests that the Ta-C (acetone) bond is more readily cleaved by H_2. Therefore, it may also react more rapidly with CO to give **5** rather than **4**. We have not yet isolated **7** since it decomposes (apparently bimolecular) in solutions more concentrated than ~0.02 M[18] to give methane and unidentified organometallic products.

This model study suggests that reductive coupling of CO with H_2 to give two carbon products might plausibly proceed via CO insertion into the metal-carbon bond of an η^2-formaldehyde ligand[9] or by coupling a formyl and an η^2-formaldehyde ligand. We are attempting to prepare η^2-formaldehyde analogues of **2** in order to see if such expectations are realistic.

Acknowledgments. We thank the Department of Energy for support (Contract No. ER-78-S-02-4949), the Francis N. Bitter National Magnet Laboratory for use of their high-field NMR facilities, G. M. Whitesides for use of his GC/MS facilities, and Scott Rocklage for preparing **7** with D_2.

References and Notes

(1) Pruett, R. L.; Walker, W. E. German Offen. 2 262 318, 1973; U.S. Appl. 210 538, 1971.

(2) (a) Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977,** *99*, 2796. (b) Shoer, L. I.; Schwartz, J. *Ibid.* **1977,** *99*, 5831–5832.

(3) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

(4) More conventional coupling schemes can be found in review articles.[5]

(5) Masters, C. A. *Adv. Organomet. Chem.* **1979,** *17*, 61 and references therein.

(6) This pentane-soluble, sublimable, yellow complex can be prepared straightforwardly from $Ta(\eta^5\text{-}C_5Me_5)Me_3Cl$ and LiMe or MeMgX in ether. $Ta(\eta^5\text{-}C_5Me_5)Me_3Cl$ is prepared from $TaMe_3Cl_2$ and LiC_5Me_5 in ether. Cf. $Ta(\eta^5\text{-}C_5H_5)Me_3Cl$: Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978,** *100*, 2389–2399.

(7) The reaction of CO with several transition metal alkyl complexes is known to yield ketones,[8] but in no such case so far has an η^2-ketone complex been observed. However, a stable η^2-formaldehyde complex has now been prepared from $Os(CO)_2(PPh_3)_3$ and formaldehyde.[9]

(8) (a) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972,** 654. (b) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968,** *41*, 750–757. (c) Shore, N. E.; Ilenda, C.; Bergman, R. G. *J. Am. Chem. Soc.* **1976,** *98*, 7436–7438. (d) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978,** 1139–1143.

(9) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505.

(10) (a) Calcd for $TaC_{15}H_{27}O$: C, 44.56; H, 6.72; mol wt, 404 (in cyclohexane). Found: C, 43.93; H, 6.79; mol wt, 412. It sublimes at 60–90 °C and 0.1-μ without change. (b) ^1H NMR (τ, tol-d_8): 8.17 (s, 6, Me_2CO), 8.34 (s, 15, C_5Me_5), 9.93 (s, 6, TaMe). ^{13}C NMR (ppm, C_6D_6, ^1H gated decoupled): 115 (s, C_5Me_5), 111 (s, $Me_2\mathit{C}O$), 55.6 (q, TaMe, $^1J_{CH} = 119$ Hz), 28.1 (q, Me_2CO, $^1J_{CH} = 122$ Hz), 10.7 (q, $C_5\mathit{Me}_5$, $^1J_{CH} = 127$ Hz).

(11) (a) The acetone methyl peak in the ^{13}C NMR spectrum of **2-****C* is a doublet with $J_{C\cdot C} = 39$ Hz, a typical[11b] $C(sp^3)–C(sp^3)$ coupling constant. (b) Axenrod, T.; Webb, G. A. "Nuclear Magnetic Resonance Spectroscopy of Nuclei other than Protons"; Wiley: New York, 1974; p 187–218.

(12) Analyses of air- and moisture-sensitive compounds are characteristically low (see the results for **2**[10a]). We think that, because **3** is especially sensitive to water, analyses have been less successful than normal. Calcd for $TaC_{16}H_{27}O_2$: C, 44.45; H, 6.29. Found: C, 43.67; H, 6.01.

(13) ^1H NMR (τ, $CDCl_3$): 8.04 (s, 15, C_5Me_5), 8.35, 8.37, 8.50 (s, 3 each, methyl groups on enolate ligand), 9.85 (s, 3, TaMe). ^{13}C NMR (ppm, $CDCl_3$, ^1H gated decoupled): 149 (s, $OMe\mathit{C}{=}CMe_2$), 119 (s, C_5Me_5), 102 (s, $OMeC{=}\mathit{C}Me_2$), 37.1 (q, TaMe, $^1J_{CH} = 121$ Hz), 19.1, 17.7, 17.5 (q, methyl groups on enolate ligand, $^1J_{CH} = 126$ Hz), 10.5 (q, $C_5\mathit{Me}_5$, $^1J_{CH} = 128$ Hz).

(14) The ^1H NMR spectrum of **3-****C,C* shows that the peaks at 8.35 and 8.50 are due to $O(Me)C{=}{}^*C\mathit{Me}_2$ ($^2J_{H\cdot C} = 6$ Hz). In the ^{13}C NMR spectrum the peaks at 19.1 and 17.7 are associated with these methyl groups ($J_{C\cdot C} = 43$ Hz and 44 Hz, respectively). The peak at 102 is due to $O(Me)C{=}{}^*\mathit{C}Me_2$ and that at 149 to $O(Me)\mathit{C}{=}{}^*CMe_2$ with $^1J_{C\cdot C} = 88$ Hz.

(15) Enolate ligands bound to Ta are produced with $Ta(CH_2CMe_3)_3(CHCMe_3)$ reacts with acyl chlorides.[16] The IR and ^1H NMR characteristics and hydrolysis products parallel those found for **3**.

(16) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978,** *100*, 3559–3568.

(17) ^1H NMR (τ, C_6D_6): 5.41 (sept, 1, $OC\mathit{H}Me_2$ $^3J_{HH} = 6$ Hz), 7.97 (s, 15, C_5Me_5), 8.72 (d, 6, $OCH\mathit{Me}_2$, $^3J_{HH} = 6$ Hz), 9.15 (d, 6, TaMe, $^3J_{HH} = 3$ Hz). The hydride peak has not yet been located. IR (solution): $\nu_{Ta\text{-}H}$ 1730 cm^{-1}. (These assignments were confirmed by preparing 7 with D_2.[18]) The trans configuration shown in eq 3 is arbitrary.

(18) Rocklage, S., unpublished results.

(19) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978.

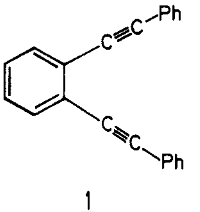
C. D. Wood, R. R. Schrock*[19]
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received March 22, 1979

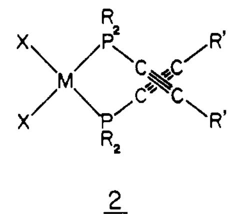
Coupling of Acetylenes Held Proximate to a Metal: Alkyne–Alkyne Interactions in *cis*-Phosphinoacetylene Complexes

Sir:

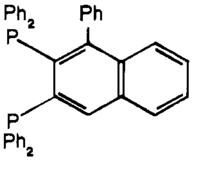
Unusual chemical reactivity, particularly toward inter- and intramolecular coupling, is often associated with aromatic diacetylenes such as **1** in which the two alkynyl groups are held rigidly adjacent to one another.[1,2] During our studies on the synthetic utility of coordinated heteroatom functionalized acetylenes,[3] we discovered a novel method to achieve the proximity of alkyne triple bonds necessary to promote coupling. Thus in cis transition metal complexes of phosphorus coordinated alkynyl phosphines, for example **2** (M = Pd, Pt; X = Cl; R = R′ = Ph), the sterically less demanding -C≡CR′ groups are forced into a configuration facilitating alkyne–alkyne interaction. We have established the nature of these unusual alkyne–alkyne contacts via a single-crystal X-ray analysis of



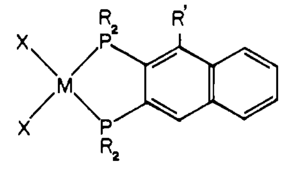
1



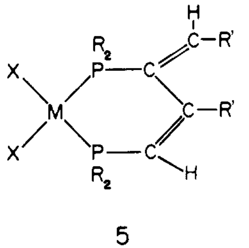
2



3



4



5

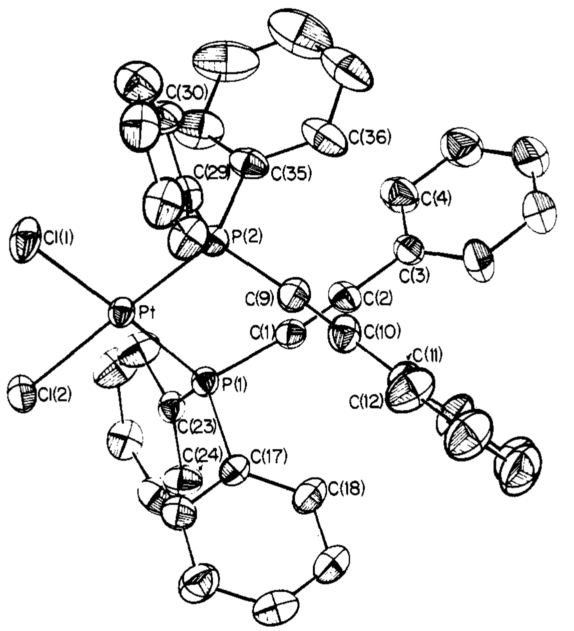


Figure 1. The molecular structure of *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2{\cdot}2CH_3CN$ drawn to illustrate the interaction between alkynyl groups. Ellipsoids represent 30% probability. Solvent of crystallisation is not shown.

cis-$PtCl_2(Ph_2PC{\equiv}CPh)_2$ and confirmed that thermal conversion of **2** (R = R′ = Ph; M = Pt; X = Cl, Br, NCS; M = Pd; X = Cl) into derivatives of the new unsymmetrical diphosphine ligand, 1-phenyl-2,3-bis(diphenylphosphino)naphthalene (**3**), is a facile, high-yield process. The concept of promoting alkyne–alkyne interactions via heteroatom coordination to a metal has potential not only for the synthesis of unsymmetrical diphosphines with an aromatic backbone[4] and their complexes but also as a general strategy for acetylene elaboration.

The cis square-planar complex **2** (M = Pt; R = R′ = Ph; X = Cl)[7] is best prepared (~80%) by reaction of $(COD)PtCl_2$ (COD = 1,5-cyclooctadiene) (0.75 g) and $Ph_2PC{\equiv}CPh$ (1.5 g) in benzene (30 mL) at room temperature. For **2** (M = Pd; X = Cl; R = R′ = Ph)[7] direct reaction at 25 °C of $Ph_2PC{\equiv}CPh$ (1.5 g) with a solution obtained by dissolving $PdCl_2$ (0.88 g) in hot CH_3CN (50 mL) gives excellent yields (≥80%).[8] Crystals of a bis(acetonitrile) solvate of **2** (M = Pt; R = R′ = Ph; X = Cl) are monoclinic, space group $P2_1/c$, with $a = 11.604\ (2)$, $b = 18.416\ (5)$, $c = 19.344\ (3)$ Å; $\beta = 98.63\ (1)°$; $Z = 4$; $\rho_c = 1.496$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 38.53$ cm^{-1}; $F(000) = 1824$. The structure analysis and refinement[9] were based on the intensities of 3716 observed ($I \geq 3\sigma(I)$) countermeasured reflections for a spherical crystal of diameter 0.25 ± 0.015 mm sealed in a glass capillary. The present R value is 0.031. An ORTEP II plot (Figure 1) illustrates the nature of the interaction between the alkyne units. In the square-planar complex, the phenyl groups on phosphorus are directed away from the polyhedral edge defined by the two phosphorus atoms, while the linear alkynyl moieties "cross" one another. The close approach of the α-carbon atoms of the phenylethynyl groups is shown by the C(1)-C(9) distance (3.110 (10) Å) which is considerably less than twice the van der Waals radius of carbon (1.65–1.70 Å). For comparison we calculate a distance of ~2.82 Å between the α-acetylenic carbon atoms in *o*-bis(phenylethynyl)benzene, a molecule also activated toward alkynyl coupling.[1] A significant deviation of the acetylenes from linearity (P(1)-C(1)-C(2), 172.7 (3); P(2)-C(9)-C(10), 173.2 (4)°) accompanies the alkynyl group contacts. Seen in the light of the molecular structure, it is not surprising that, on refluxing in benzene overnight or in toluene (2 h), **2** (M = Pt; R = R′ = Ph; X = Cl) is converted in high yield (80%) into an isomeric complex **4** exhibiting no $\nu(C{\equiv}C)$ bands in the IR but retaining cis stereochemistry (ν(Pt-Cl) 317 (m), 274 (m) cm^{-1}) and with two nonequivalent phosphorus atoms (^{31}P NMR ($CDCl_3$, downfield from external 85% H_3PO_4): δ_{P_A} 44.2 ($J_{P_A\text{-}^{195}Pt} = 3499$ Hz), δ_{P_B} 35.8 ppm ($J_{P_B\text{-}^{195}Pt} = 3570$, $J_{P_A\text{-}P_B} = 7.8$ Hz). Bromide and thiocyanate analogues **4** (M = Pt; R = R′ = Ph; X = Br, NCS) were synthesized by metathesis or from **2** (X = Br, NCS) via thermolysis. The palladium complex **2** (M = Pd; R = R′ = Ph; X = Cl) could also be converted into **4**, albeit in a poorer yield (~60%) which we attribute to partial isomerization of **2** to an unreactive trans form. To distinguish the various structural possibilities for an unsymmetrical diphosphine formed via acetylene coupling, an X-ray analysis of the free ligand **3**, disengaged from **4** (M = Pt; R = R′ = Ph; X = Cl),[10] was carried out. Crystals of **3** are triclinic, space group $P\bar{1}$, with $a = 11.437\ (13)$, $b = 9.628\ (12)$, $c = 16.712\ (21)$ Å; $\alpha = 82.31\ (9)$, $\beta = 119.08\ (3)$, $\gamma = 110.03\ (5)°$; $M = 572.63$; $Z = 2$; $\rho_c = 1.259$, $\rho_m = 1.27$ g cm^{-3}; $\mu(\text{Cu K}\alpha) = 14.98$ cm^{-1}. The structure was solved and refined[9] using 1683 observed reflections to $R = 0.058$. An ORTEP II plot (Figure 2) shows that the ligand **3** is 1-phenyl-2,3-bis(diphenylphosphino)naphthalene, a rigid, chelating diphosphine with a planar aromatic backbone formed via coupling of the two α-carbon atoms of the phosphino alkynes together with attack by the β carbon of one alkyne on the ortho position of the phenyl ring on the second alkyne. It is interesting that in the free ligand the Ph_2P groups adopt a configuration which minimizes lone pair–lone pair repulsions *and* steric interactions between phenyl substituents. Nevertheless, nonbonded repulsions between PPh_2 groups may account for some distortion of angles subtended at the phenyl substituents: P(1)-C(17)-C(18), 125.8 (3); P(1)-C(23)-C(28), 125.7 (3), P(2)-C(35)-C(36), 126.8 (3)°.

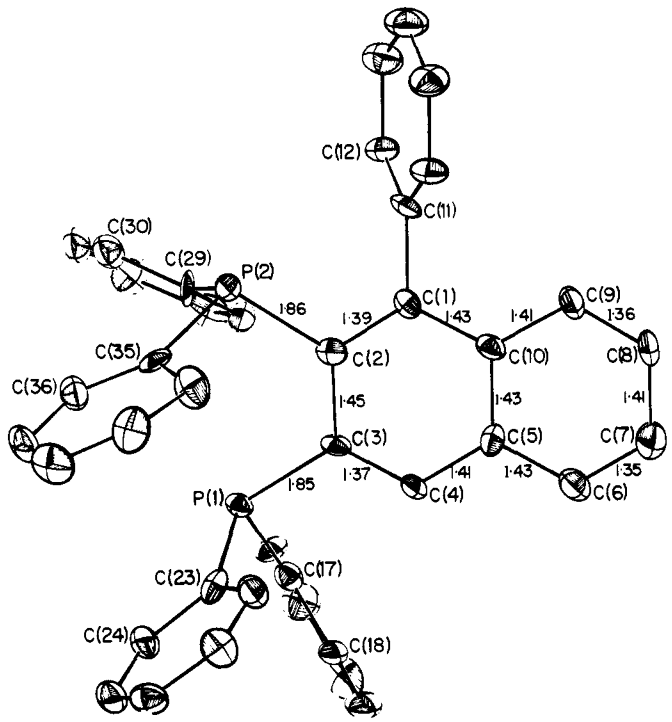


Figure 2. A perspective ORTEP II drawing of the structure of 1-phenyl-2,3-bis(diphenylphosphino)naphthalene. Ellipsoids are drawn at the level of 30% probability.

The precise mechanism of thermal coupling (**2** → **4**, R = R′ = Ph) has not yet been established, but it is clear that the ability of the metal to hold the acetylenes proximate plays a major role in the activation process. The favorable conformation in **2** (M = Pt; R = R′ = Ph; X = Cl) is not restricted to -C≡CPh groups. Indeed an X-ray analysis of **2** (M = Pd; R = Ph; R′ = *t*-Bu; X = CNS) has shown that, even with bulky substituents, the alkynyl groups are held adjacent.[11] The analogy with bis(phenylethynyl)benzene[1] is given further credence by the conversion of **2** (M = Pt; R = R′ = Ph; X = Cl) in moist, acidic chlorobenzene into the unsymmetrical diphosphine complex **5** in good yield, presumably via initial electrophilic attack at a β-carbon atom. We are currently exploring the wider implications of these fascinating reactions.

Acknowledgment. We are grateful to the National Research Council of Canada for financial support of this work.

Supplementary Material Available: A listing of structure factors for 1-phenyl-2,3-bis(diphenylphosphino)naphthalene ($(Ph_2P)_2C_{16}H_{10}$) and $PtCl_2(Ph_2PC{\equiv}CPh)_2 \cdot 2CH_3CN$ (29 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For example *o*-bis(phenylethynyl)benzene exhibits intramolecular interaction between the triple bonds in reactions with electrophiles or nucleophiles: H. W. Whitlock and P. E. Sandvick, *J. Am. Chem. Soc.*, **88,** 4525 (1966).

(2) Photochemical dimerization of *o*-bis(phenylethynyl)benzene yields verden, an azulene derivative, via intermolecular coupling: E. Müller, M. Sauerbier, D. Streichfuss, R. Thomas, W. Winter, G. Zountsas, and J. Heiss, *Justus Liebigs Ann. Chem.*, **750** 63 (1971).

(3) D. K. Johnson and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 903 (1977); A. J. Carty, S. E. Jacobson, R. T. Simpson, and N. J. Taylor, *J. Am. Chem. Soc.*, **97,** 7254 (1975).

(4) Although chelating ligands with R_2P or R_2As substituents on an aromatic backbone were extensively exploited in the renaissance period of inorganic chemistry, particularly by the groups of Chatt[5] and Nyholm,[6] their general utility has been severely hampered by the difficulty of their synthesis. Thus *o*-phenylenebis(diphenylphosphine) can be prepared in 1% overall yield from *o*-bromochlorobenzene in a tedious four-stage synthesis. See F. A. Hart, *J. Chem. Soc.*, 3324 (1960).

(5) J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 2537 (1962), and references therein. For a general review of bidentate phosphorus complexes, see W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, **14,** 173 (1972).

(6) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 560 (1958), and references therein.

(7) Complexes **2** have characteristic ν(M–Cl) bands for cis stereochemistry (e.g., **2** (M = Pt; R = R′ = Ph), 314 (s), 294 (s); **2** (M = Pd; R = R′ = Ph), ν(Pd–Cl) 321 (s), 300 (s) cm^{-1}) and have been analyzed satisfactorily.

(8) This is a very simple and effective route to Pd(II) halo complexes which avoids the isolation of intermediates, e.g., $PdCl_2(PhCN)_2$, $(COD)PdCl_2$.

(9) Intensity data for **2** (M = Pt; R = R′ = Ph; X = Cl) were collected on a Syntex $P2_1$ diffractometer using Mo Kα radiation with a variable scan rate. A total of 5382 independent reflections were measured. For **3** a GE-XRD-6 Datex automated instrument operating in a $\theta/2\theta$ scan mode with Cu Kα radiation was used and 2433 independent measurements were collected. In both cases the structure was solved via Patterson and Fourier methods. Refinement was by full-matrix least-squares techniques. All nonhydrogen atoms have been refined using anisotropic thermal parameters. The residual *R* is defined as $R = (\Sigma|F_o - F_c|/\Sigma|F_o|)$.

(10) Complex **4** (M = Pt; R = R′ = Ph; X = Cl) (0.5 g) and KCN (5 g) were refluxed overnight in benzonitrile (70 mL) under N_2. Following evaporation of solvent, extraction with ether, dry chromatography on Florisil, and recrystallization from CH_2Cl_2–EtOH (1:1), a mixture of needles (2,4,6-triphenyl-*s*-triazine from trimerization of PhCN, identified by mass spectrometry microanalysis, and comparison with an identical sample) and prisms **4** (~30% from **2**) were obtained.

(11) A. J. Carty, T. W. Ng, and G. J. Palenik, unpublished results.

Arthur J. Carty,* Nicholas J. Taylor
David K. Johnson
Guelph-Waterloo Centre for Graduate Work in Chemistry
Waterloo Campus, University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

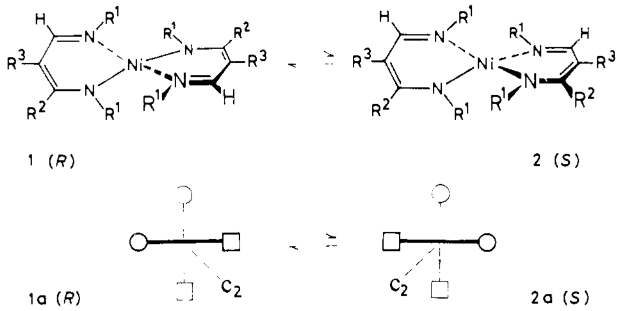
Received April 20, 1979

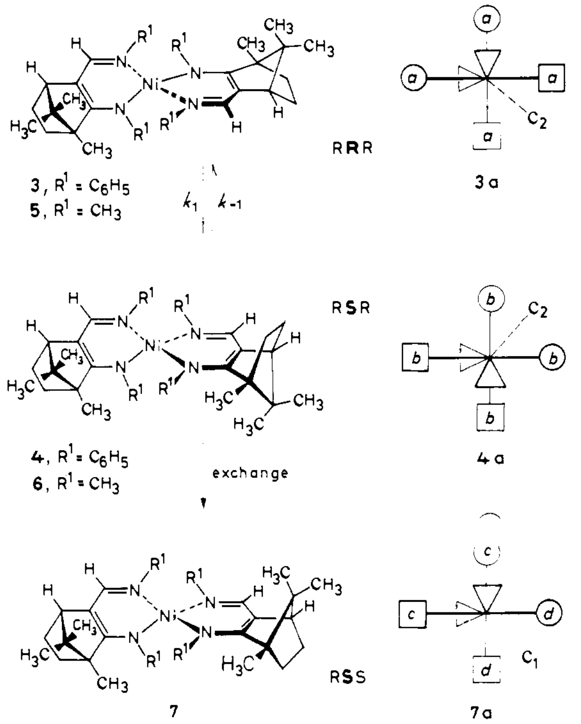
Barriers against Configurational Isomerization at Tetrahedral Nickel(II)

Sir:

Paramagnetic (d^8), pseudotetrahedral[1] nickel N_4 chelates of type **1** are configurationally stable on the NMR time scale.[2] This surprising observation has been exploited for conformational analysis[3] and for recognition of substituent rotations[4] in cases of central[2,3] and axial[2,4] chirality at nickel, ~23 kcal/mol (453 K) of free activation enthalpy[2] being required for transformation of **1** ($R^1 = C_6H_5$) into its enantiomer **2.** The C_2 symmetry of these compounds may be easily recognized from projection formulae such as **1a** and **2a,** viewing **1** as the *R* configuration and **2** as the *S* in idealized tetrahedral coordination from the right-hand side. As previously explained,[2] the more heavily substituted flanks of the chelate moieties were denoted as squares and the hydrogen sites as circles.

Since very little is known about isomerization and substitution mechanisms of open-shell, tetrahedral transition-metal complexes, a determination of the barrier against racemization (**1** ⇌ **2**) would be of obvious interest.[5] Rather than trying to resolve a racemic mixture, we chose to tackle this problem by the technique of chiral, nonracemizable anchor groups in **3.** The required ligands were prepared from optically active (*R*)-camphor[6] in the usual way.[7,8] In the isomer drawn as **3,** the configuration at nickel[9] was denoted by the central ***R*** in *R**R**R*. Inversion at the central metal will produce **4** with *R**S**R* configuration. Both of these diastereomers are chiral and of C_2 symmetry, as is easily seen from projections **3a** and **4a** where the wedges indicate orientations of the isopropylidene bridges. The overall structure is fully (pseudo)tetrahedral between −80 and +137 °C in $Cl_2CD\text{-}CDCl_2$ or tetralin as shown by the paramagnetism[10] and temperature-independent reduced shifts.[11]


1 (*R*) 2 (*S*)
1a (*R*) 2a (*S*)


3, $R^1 = C_6H_5$
5, $R^1 = CH_3$
4, $R^1 = C_6H_5$
6, $R^1 = CH_3$
7
3a
4a
7a

The interconversion of **3** and **4** was measured by integration of the two NMR signals for the two pairs of symmetry-related p-hydrogen atoms[12] of **3** (phenyl groups a in **3a**), as well as by