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.

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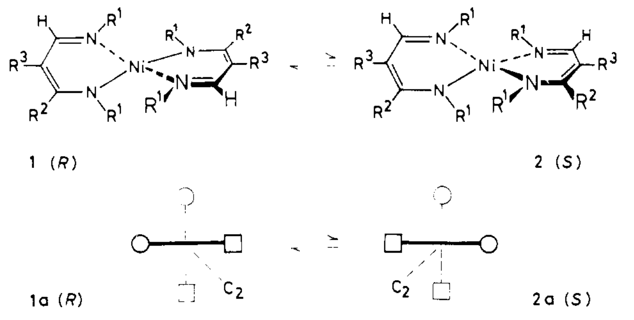
Barriers against Configurational Isomerization at Tetrahedral Nickel(II)

Sir:

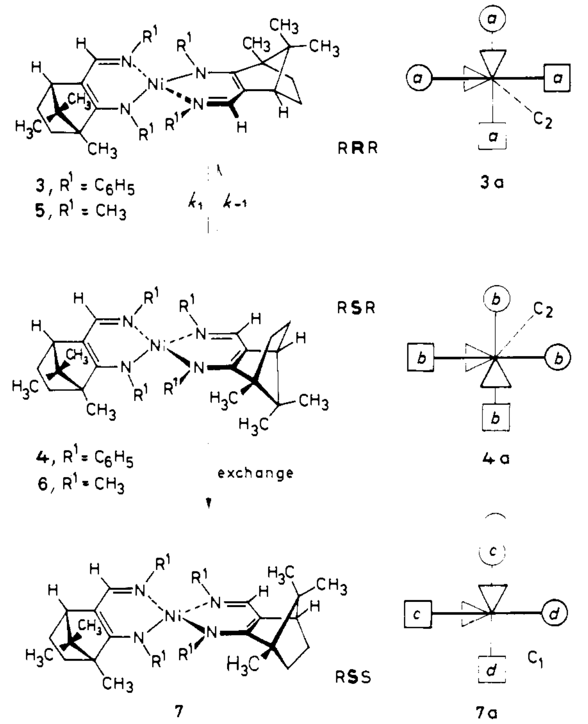
Paramagnetic (d^8), pseudotetrahedral[1] nickel N_4 chelates of type **1** are configurationally stable on the NMR time scale.[2] This surprising observation has been exploited for conformational analysis[3] and for recognition of substituent rotations[4] in cases of central[2,3] and axial[2,4] chirality 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-$CDCl_2$ 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, $R^1 = CH_3$

RRR 3a

k_1 k_{-1}

4, $R^1 = C_6H_5$
6, $R^1 = CH_3$

RSR 4a

exchange

7 RSS 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 the observation of two new, corresponding signals[12] of **4** (b in **4a**). On the other hand, **3** and **4** behave like enantiomers in their chiroptical properties with respect to nickel, i.e. $[\theta]_{630}$ ca. −1190 and +1260. Therefore, the diastereomerization **3** → **4** can also be monitored by time-dependent circular dichroism (mutarotation). The interconversion rates are cleanly first order for **3** in tetralin solution; both methods define a common Eyring plot with $\Delta H^{\ddagger} = 22.5\ (\pm 0.8)$ kcal/mol and $\Delta S^{\ddagger} = -15\ (\pm 3)$ cal K^{-1} mol^{-1}. The $\Delta G^{\ddagger}$ values of 27.0 (at room temperature) or 29.3 kcal/mol (at 453 K for comparison with **1**) thus confirm the lower limit[2] of ≥21.8 kcal/mol for **1** ($R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = C_2H_5$).

Does the bulky bornane skeleton perturb such barriers? We measured the inversion **5** ⇌ **6** for comparison with the known[2] activation enthalpy 17.3 kcal/mol (at 358 K in cyclohexane) of **1** ($R^1 = R^2 = CH_3$, $R^3 = C_2H_5$). Both processes are fast on the NMR time scale and can be followed by coalescence studies on several pairs of diastereotopic protons. Although **5–6** is too sensitive to be isolated in pure form, its very large and characteristic chemical ^1H NMR shifts permit the easy evaluation of $\Delta G^{\ddagger} = 17\ (\pm 1)$ kcal/mol (at 345 K in benzene–tetralin). Thus at least for $R^1 = CH_3$ the comparison of **5–6** with the above **1** shows no distinct perturbation by the bornane moiety.

Barriers of such heights are very unusual[13] for open-shell tetrahedra. When diastereomerization of **3** was performed in the presence of racemic ligand, the third possible, completely asymmetric (C_1 in **7a**) diastereomer **7** was also observed[12,14] as *R**RS*** (and/or its antipode[2] *RSS*). Both **4** and **7** NMR signals appear with comparable rates but now somewhat faster than in the absence of free ligand. Since **7** can be formed from **3** only by ligand exchange, it is clear that substitution can be faster than configurational inversion. Some mechanistic features of these competing pathways will be published shortly.

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(6) *R* is used as a simplified notation for the 1*R*:4*R* configuration of *d*-(+)-camphor.
(7) McGeachin, S. G. *Can. J. Chem.* **1968,** *46,* 1903–1912.
(8) Structural assignments of these compounds were based on full spectroscopic characterization and correct elemental analyses.
(9) Configurational assignments at nickel are arbitrary but in no way relevant for the conclusions drawn here.
(10) Optically active **3** crystallized in pure form from ethyl acetate–ethanol: mp 187–189 °C; molecular mass (benzene) calcd 718, found 690; magnetic dipole moment, found 3.14 μ_B in $(Cl_2CD)_2$ at 26 °C.
(11) Knorr, R.; Polzer, H.; Bischler, E. *J. Am. Chem. Soc.* **1975,** *97,* 643–644.
(12) The reduced NMR shifts[11] of these 4-H's are ϑ +25.7 and +29.3 ppm for **3,** +27.0 and +28.3 ppm for **4,** +26.4 and +30.5 ppm for **7.**
(13) See ref 2 and 5 for some relevant references.
(14) The resultant mixture showed the same NMR shifts as a solution of the nickel complex[8] (mp 237.5–239 °C) prepared from the racemic ligand.

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Time-Resolved CIDEP and ESR Studies of Heavy Metal–Organic Radical Complexes. The Uranyl–Phenanthroquinone Radical Ions

Sir:

The rather turbulent debate as to the origins of the CIDEP (chemically induced dynamic electron polarization) observed in the ESR spectra of photogenerated radicals has abated, and, as it is now generally accepted that there are two distinctly different mechanisms,[1] interest has turned to chemical applications. While almost all of the CIDEP initial polarization systems reported to date involve the photochemical triplet of organic carbonyl compounds,[1] our recent efforts in CIDEP applications have been mainly directed towards metal–quinone complexes, particularly the *o*-phenanthroquinone (PQ).[2] We report here our first successful application of time-resolved CIDEP to heavy metal–organic radical complexes: the uranyl–phenanthroquinone radical ions. Historically the photochemistry of uranyl ion has played an important role[3] in the development of modern photochemistry. The CIDEP results will shed some light on the primary photochemical processes of uranyl ions and the ESR characterization of the uranyl–quinone complex ions should be of wider interest to chemistry in general.

The laser flash photolysis (Molectron 1-MW N_2 pulsed laser) and the time-resolved dc detection CIDEP observation system were assembled similarly to those reported by Kim and Weissman.[4] The total spectrometer dc response time was measured and found to be 0.2 μs. A detailed examination of the system performance and the analysis of the relaxation measurements will be described elsewhere.

When a degassed THF containing 10^{-3} M each of PQ and $UO_2(NO_3)_2 \cdot 6H_2O$ was exposed briefly to light in the ESR cavity with 100-kHz modulation at −60 °C, a well-resolved spectrum was observed (Figure 1A). Prolonged UV irradiation led to the disappearance of the spectrum and in its place a new spectrum (Figure 1B) was developed when irradiation was terminated. Both spectra are characterized by a distinctly low *g* factor and their ESR parameters are given in Table I. The analyses of the hyperfine structures are consistent with the assignments of $[UO_2PQ]^{+\cdot}$ and $[UO_2HPQ]^{2+\cdot}$, respectively, in which the unpaired spin is associated mainly with the phenanthroquinone moiety. The low *g* factor can be explained by the coordination to the uranium nucleus having a large spin–orbit coupling. Hyperfine interaction due to ^{235}U ($I = 7/2$,

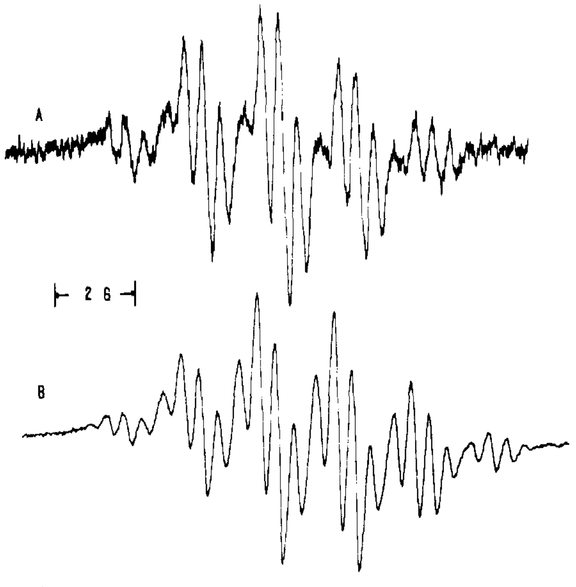

Figure 1. ESR spectra of (A) $[UO_2PQ]^+$ in THF at −60 °C, (B) $[UO_2HPQ]^{2+}$ in THF at −60 °C.