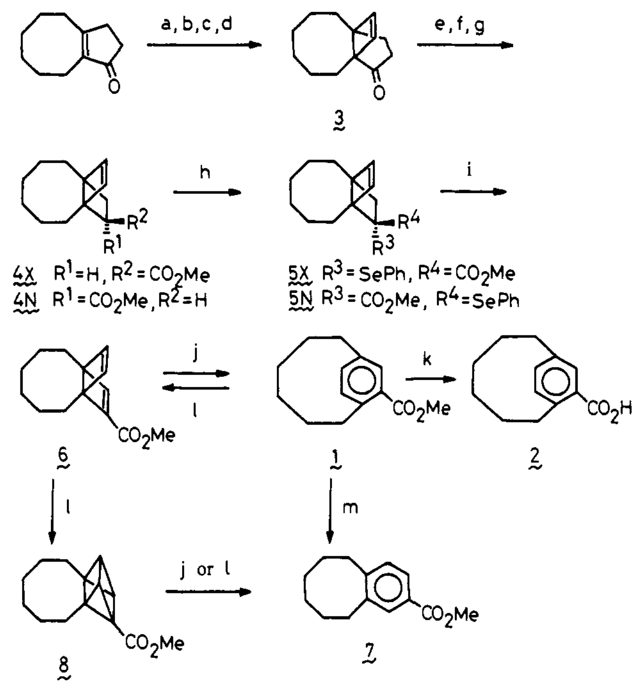
Scheme I



[a] Dichloroethylene (cis-trans mixture), $h\nu$, Pyrex. [b] $HOCH_2CH_2OH$, H_2SO_4, C_6H_6. [c] Na, NH_3, Et_2O. [d] 1.2 N HCl, Et_2O. [e] HCO_2Et, EtONa, Et_2O. [f] TsN_3, Et_3N, CH_2Cl_2. [g] $h\nu$, Pyrex, MeOH. [h] LDA, Ph_2Se_2, THF. [i] H_2O_2, pyridine, CH_2Cl_2. [j] Heat. [k] KOH, MeOH. [l] $h\nu$, Pyrex, hexane. [m] $h\nu$, quartz, hexane.

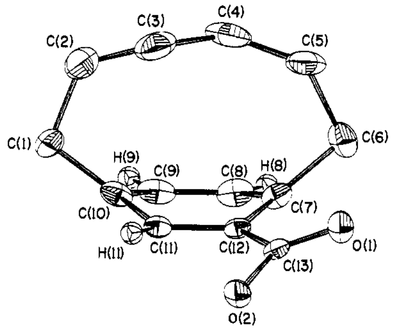
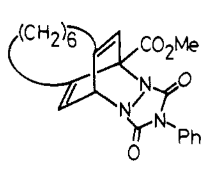


Figure 1. Molecular structure of **2**. Non-hydrogen atoms are drawn by the thermal ellipsoids at the 20% probability level. Hydrogen atoms are shown by the spheres corresponding to the artificial isotropic temperature factor of 1.0 Å^{-2}.

most remarkable structural feature of **2** is, of course, the distortion of the benzene ring from planarity: the para carbons (C(7) and C(10)) are lifted out of the plane of the other four benzene carbons (C(8), C(9), C(11), and C(12)) by 21.1 and 20.3°, respectively. The benzyl carbons (C(1) and C(6)) are out of the planes of C(9)–C(10)–C(11) and C(8)–C(7)–C(12) by 17.4 and 20.2°, respectively. Comparison of these values with those of 3-carboxy[7]paracyclophane (α_{av} = 16.8°, β_{av} = 6.8°)[2b] clearly indicates that the out-of-plane deformation, especially that of the benzyl carbons, is significantly greater in the smaller bridged compound. Moreover, the bond angles of the side chain (C(2), C(3), C(4), C(5)) are considerably widened from the normal C(sp^3)–C(sp^3)–C(sp^3) bond angle (average 126.5°), even if one takes into account the inaccuracy of the data due to the thermal motion of the bridge.[7]

Interestingly, it was found that the photochemical valence isomerization of **1** takes place stepwise in the sequence **1** → **6** → **8** → **7** (Scheme I): irradiation of a hexane solution of **1** with a high-pressure mercury lamp in a quartz vessel gave the benzocyclooctene **7** in 47% isolated yield as a single product. Irradiation through a Pyrex filter, however, led to rapid formation of the Dewar isomer **6**. When irradiation of **6** was continued under the above conditions, slow conversion to the prismane derivative **8** was observed. Further irradiation of **8** furnished **7**.

Furthermore, treatment of **1** with a dienophile such as *N*-phenyl-1,2,4-triazoline-3,5-dione afforded two kinds of [4 + 2] cycloadducts, **9** and **10**, in a ratio of 1:2. The details will be reported shortly.



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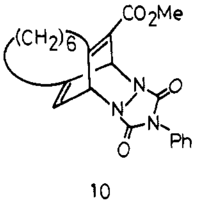

10

Registry No. 1, 84538-15-8; **2**, 84538-16-9; **3**, 84538-10-3; α-diazo-3, 84538-11-4; **4X**, 84538-12-5; **4N**, 84620-30-4; **5X**, 84538-13-6; **5N**, 84620-31-5; **6**, 84538-14-7; Ph_2Se_2, 1666-13-3; *cis*-dichloroethylene, 156-59-2; *trans*-dichloroethylene, 156-60-5; 2,3,4,5,6,7,8,9-octahydro-1*H*-cyclopentacycloocten-1-one, 38262-50-9.

Supplementary Material Available: Listing of the spectral and analytical data of new compounds and Table S1 listing the fractional atomic coordinates (6 pages). Ordering information is given on any current masthead page.

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(5) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN-78: A System Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and Louvain, Belgium, 1978.

(6) Ashida, T. "HBLS-V: The Universal Crystallographic Computing System-Osaka"; The Computation Center, Osaka University, 1979.

(7) In order to obtain more detailed information on the structure of the bridging chain, a low-temperature structure determination is now being performed, and the results will be published elsewhere.

(8) Johnson, C. K. "ORTEP-II"; Report ORNL-5138. Oak Ridge National Laboratory, TN, 1976.

Isolable Species from Nucleophilic Attack at Sulfinyl and Sulfonyl Sulfur: A Sulfurandioxide (10-S-5)[1] Salt and a Sulfuranoxide (10-S-4)[1] Salt

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Received September 20, 1982

Mechanisms of nucleophilic attack at sulfinyl[2] and at sulfonyl[3] sulfur have been exhaustively studied. Evidence has been sought to support a choice between (a) a two-step process, via sulfurane intermediates, and (b) a one-step concerted (S_N2) process. A recent review[4] has championed the first mechanism, a, to explain

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(1) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(2) (a) Bunton, C. A.; de la Mare, P. D. B.; Greasely, P. M.; Llewellyn, D. R.; Pratt, N. H.; Tillet, J. G. *J. Chem. Soc.* **1958**, 4751. (b) Biasotti, J. B.; Andersen, K. K. *J. Am. Chem. Soc.* **1971**, *93*, 1178. (c) Kice, J. L.; Walters, C. A. *Ibid.* **1972**, *94*, 590. (d) Senatore, L.; Cuiuffarin, E.; Fava, A.; Levita, G. *Ibid.* **1973**, *95*, 2918. (e) Kice, J. L.; Puls, A. R. *Ibid.* **1977**, *99*, 3455. (f) Najam, A. A.; Tillett, J. G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 858.

(3) (a) Graafland, T.; Nieuwpoort, W. C.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1981**, *103*, 4490. (b) Laleh, A.; Ranson, R.; Tillett, J. G. *J. Chem. Soc., Perkin Trans 2* **1980**, 610. (c) Kaiser, E. T. *Acc. Chem. Res.* **1970**, *3*, 145. (d) Deacon, T.; Farrar, C. R.; Sikkel, B. J.; Williams, A. *J. Am. Chem. Soc.* **1978**, *100*, 2525. (e) Rogne, O. *J. Chem. Soc., Perkin Trans 2* **1975**, 1486. (f) Ciuffarin, E.; Senatore, L.; Isola, M. *Ibid.* **1972**, 468. (g) Vizgert, R. V. *Russ. Chem. Rev.* **1963**, *32*, 1. (h) Aberlin, M. E.; Bunton, C. A. *J. Org. Chem.* **1970**, *35*, 1825.

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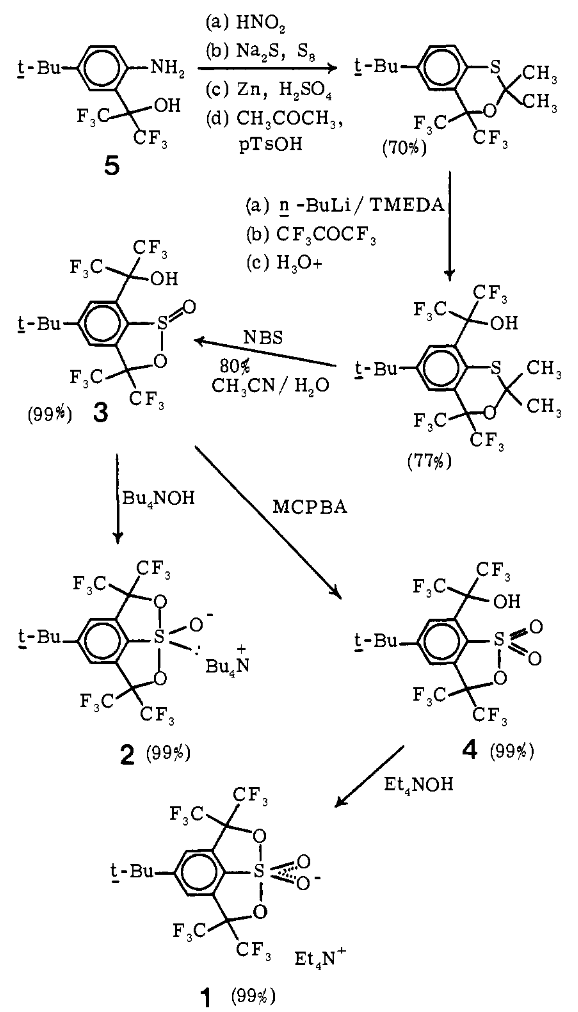
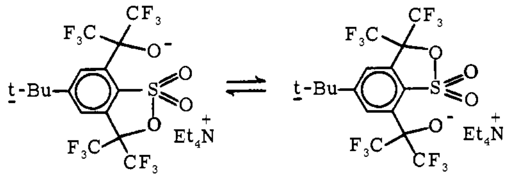
Scheme I



all the evidence reported by proponents of either process. We report the preparation and characterization of 10-S-5 sulfurandioxide salt, **1**,[5] the first example of an observable analogue to the intermediate postulated to lie along the pathway of associative nucleophilic attack at sulfonyl sulfur. The 10-S-4 sulfuranoxide, **2**,[6] analogue of the postulated intermediate in nucleophilic reactions at sulfinyl sulfur was also prepared. The syntheses from the previously described[7] precursor **5** are outlined in Scheme I.

Our choice of symmetrical 10-S-5 structure **1**, over the alternative formulation as a rapidly equilibrating mixture of **1a** and **1b**, is based on low-temperature NMR studies and pK_a measurements.[8]



1a **1b**

The ^{19}F NMR spectrum (338 MHz) of anion **1** has only a single sharp singlet at −90 °C, and the ^{1}H NMR spectrum (220 MHz) exhibits only one aromatic proton peak at −85 °C. In contrast, the ^{19}F NMR spectrum of conjugate acid **4**[9] shows two singlets, and the ^{1}H NMR spectrum shows two broad singlets in the aromatic proton region. The low-temperature NMR spectra of the sulfurandioxide anion are, of course, consistent with either the closed structure, **1**, or a very rapid equilibration between **1a** and **1b**.

The pK_a for the hypothetical equilibrium between alcohol **4** and the open-chain alkoxide **1a** was estimated, using a Hammett treatment for the acidity of ring-substituted hexafluorocumyl alcohols, to be 9.4 (at 25 °C).[10] The value of pK_a measured titrimetrically (7.2) is substantially lower, implying a substantial stabilization of the conjugate base by the bridging to hypervalent sulfur in **1**. The closed form of anion **1** is at least ca. 3.0 kcal/mol more stable than the open-chain isomer **1a**.

Using a parallel approach, we have established the ring-closed structure **2** as the correct formulation of the 10-S-4 sulfuranoxide salt, ruling out the open-chain sultine alkoxide analogous to sultone alkoxides **1a** and **1b**. The 338-MHz ^{19}F NMR spectrum of anion **2**[6] shows evidence of only two types of CF$_3$ groups (two quartets) at −90 °C. The 220-MHz ^{1}H NMR spectrum shows only a sharp singlet in the aromatic region at −85 °C. These data are all consistent with the closed structure (**2**). In contrast, the low-temperature ^{19}F NMR spectrum of alcohol **3**[11] allows assignment of four CF$_3$ groups even though the room-temperature (85 MHz) ^{19}F NMR spectrum shows only two quartets. The 338-MHz ^{19}F NMR data indicate that the interconversion of **3** and its enantiomer formed by nucleophilic attack at sulfur occurs with $\Delta G^*_{25} = 13$ kcal/mol.[12]

The sultine alcohol, analogous to **3**, in which CF$_3$ groups are replaced by CH$_3$ groups was described earlier.[13a] Its NMR spectrum[13b] reflects structural features for the alcohol and its conjugate base parallel to those described for **3**. In this case as well, the apparent symmetry evidenced in the NMR spectrum of the anion could be the consequence of either a symmetrical sulfuranoxide ground state or a very low-energy barrier for the interconversion of the unsymmetrical alkoxides.

The first unequivocal evidence for a 10-S-4 sulfuranoxide anion is based on the comparison of the titrimetrically measured pK_a of **3** (5.0) with the value estimated[10] for its equilibrium with the corresponding open-chain alkoxide salt (9.6). The difference in calculated and observed pK_a values indicates that the correct formulation of the conjugate base of **3** (for reasons analogous to those given for **1**) is the closed form **2**. This difference also implies that the closed structure **2** is at least 6.3 kcal/mol more stable than its open-chain sultine alkoxide isomer.

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(5) Compound **1**: mp 196–196.5 °C; ^{19}F NMR (25 °C; 338 MHz, CD_3COCD_3) δ −74.9 (s, 6, CF$_3$); ^{19}F NMR (−90 °C; 338 MHz, CD_3COCD_3) δ −74.9 (s, 6, CF$_3$); ^{1}H NMR (25 °C; CD_3COCD_3) δ 1.4 (t, 12, $J_{HH} = 7$ Hz, CH$_3$), 1.5 (s, 9, CH$_3$), 3.5 (q, 8, $J_{HH} = 7$ Hz, CH$_2$), 7.9 (s, 2 Ar H). Anal. ($C_{24}H_{31}F_{12}NO_4S$) C, H, F, N, S. All ^{19}F NMR chemical shifts are reported in ppm downfield from CFCl$_3$. All ^{1}H NMR shifts are in ppm downfield from Si(CH$_3$)$_4$.

(6) Compound **2**: mp 128–129 °C; ^{19}F NMR (25 °C; 338 MHz, CD_3COCD_3) δ −74.3 (q, 6, $J_{FF} = 9$ Hz, CF$_3$), −75.7 (q, 6, $J_{FF} = 9$ Hz, CF$_3$); ^{19}F NMR (−90 °C; 338 MHz, CD_3COCD_3) δ −74.4 (br, m, 6, CF$_3$), −75.5 (br m, 6, CF$_3$); ^{1}H NMR (CD_3COCD_3) δ 0.95 (t, 12, CH$_3$), 1.39 (s, 9, CH$_3$), 1.45 (m, 8, CH$_2$), 1.87 (m, 8, CH$_2$), 3.46 (m, 8, CH$_2$), 7.8 (s, 2, Ar H). Anal. ($C_{32}H_{47}F_{12}NO_3S$) C, H.

(7) Amey, R. L. Ph.D. Thesis, University of Illinois, Urbana, IL, 1979.

(8) After this paper was first submitted, we completed an X-ray structure for **1** that confirmed, for the solid state, the structure postulated in this paper for **1** in solution. Refinement to an R value of 0.046 reveals a slightly distorted trigonal-bipyramidal structure with an apical O–S–O angle of 167.69 (9)°, apical S–O bond lengths of 1.972 (2) and 1.930 (2) Å, and equatorial S–O bond lengths of 1.417 (2) and 1.426 (2) Å. An X-ray structure of the tetraethylammonium analogue of sulfuranoxide salt **2** is in progress. These will be reported in the full paper (Perkins, C. W.; Wilson, S. R.; Martin, J. C., to be submitted for publication.

(9) Compound **4**: mp 202–204 °C; ^{19}F NMR (CDCl$_3$) −75.0 (s, 6, CF$_3$), −75.4 (s, 6, CF$_3$); ^{1}H NMR (CDCl$_3$) δ 1.4 (s, 9, CH$_3$), 7.8 (br s, 1, Ar H), 8.0 (br s, 1, Ar H). Anal. ($C_{16}H_{11}F_{12}O_4S$) C, H.

(10) The pK_a values were calculated by applying estimated Hammet σ values for the ρ value (1.1) determined for measured acidities of para-substituted hexafluorocumyl alcohol. Some of the preliminary Hammet studies were carried out by Dr. M. Ross using 50% ethanol/H$_2$O at 25 °C.

(11) Compound **3**: mp 203–205 °C; ^{19}F NMR (25 °C; CDCl$_3$) δ −74.5 (q, 6, $J_{FF} = 9$ Hz, CF$_3$), −75.9 (q, 6 $J_{FF} = 9$ Hz, CF$_3$); ^{19}F NMR (−50 °C; 338 MHz, CD_3COCD_3) δ −74.4 (br s, 3, CF$_3$), −74.6 (br s, 3 CF$_3$), −74.9 (br s, 3, CF$_3$), −75.9 (br s, 3 CF$_3$); ^{1}H NMR (CD_3COCD_3) δ 1.4 (s, 9, CH$_3$), 5.6 (s, 1, OH), 8.1 (s, 2, Ar H). Anal. ($C_{16}H_{11}F_{12}O_3S$) C, H.

(12) The ΔG^*_{25} was approximated by using the NMR data from the near-exchange region and the Gutowsky-Holm equation. Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(13) (a) Lau, P. H. W.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7077. (b) Lau, P. H. W. Ph.D. Thesis, University of Illinois, Urbana, IL 1979.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (NSF CHE 81-13142). The NMR spectra reported were provided by the University of Illinois Midwest National Science Foundation Regional NMR Facility (CHE 79-16100). Mass spectra were obtained from facilities provided under grants from the National Institutes of Health (CA 11388 and GM 16864).

Unique Stable Organometallic Nickel(III) Complexes: Syntheses and the Molecular Structure of Ni[$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′]I_2

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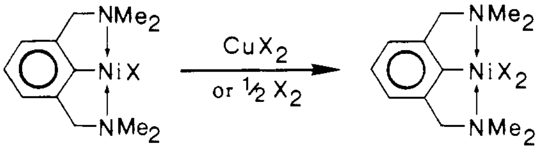
Received September 1, 1982

There are several reports of stable paramagnetic organo transition-metal species in which there is a direct metal–carbon interaction.[1] However, the metals of the nickel triad are poorly represented, and those examples known for nickel almost invariably contain cyclopentadienyl, carbaborane, cyano, or CO moieties.[2,3] We now report the preparation of a unique series of organometallic Ni(III) complexes of general formula Ni[$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′]X_2 (**1a–c**, X = Cl, Br, I), in which the square-pyramidal metal coordination sphere comprises two halo atoms (one apical), two N donor atoms, and most importantly a direct Ni–C σ bond to an aryl function.

The reaction of diamagnetic square-planar Ni[$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′]X **2a–c**,[4] X = Cl, Br, I, with an appropriate reagent ($CuCl_2$, $CuBr_2$, I_2) affords the new complexes **1a–c** in high yield[5] (eq 1). These almost black solid paramagnetic[6] complexes



(1)

2 a X = Cl, b X = Br, c X = I.

1 a X = Cl, b X = Br, c X = I.

are air-stable and are reasonably soluble in CH_2Cl_2 and sparingly soluble in toluene to afford brown-yellow, green, and red-violet solutions for **1a**, **1b**, and **1c**, respectively.[7] The ESR spectrum (X band) of each of these monomeric complexes at room temperature shows a single broad absorption signal[8] (lacking hyperfine structure) which at ~–140 °C (toluene glass) becomes an orthorhombic signal with three distinct *g* values. As an example, that of the chloro derivative **1a** is shown in Figure 1 ($g_\parallel = 2.020$, $g_\perp = 2.190$, $g_\perp' = 2.366$), and here only the $g_\parallel$ tensor shows hyperfine coupling consistent with coupling of the electron to a single Cl atom; A = 28 G. The diiodo and dibromo analogues give comparable signals with the hyperfine coupling on the $g_\parallel$ tensor being approximately 140 and 150 G, respectively. However, these latter spectra possess hyperfine structure on the $g_\perp$ tensor also, and second-order hyperfine interactions are present since the hyperfine components of the parallel and perpendicular regions are not separated.[9] These data taken together with the absence of ^{14}N coupling suggest that the unpaired electron does not lie in an orbital in the plane of the coordinated [$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′] skeleton but is probably localized in a unique metal–halogen orbital. To definitively establish the nature of these complexes, an X-ray crystallographic study has been carried out on **1c** (X = I).

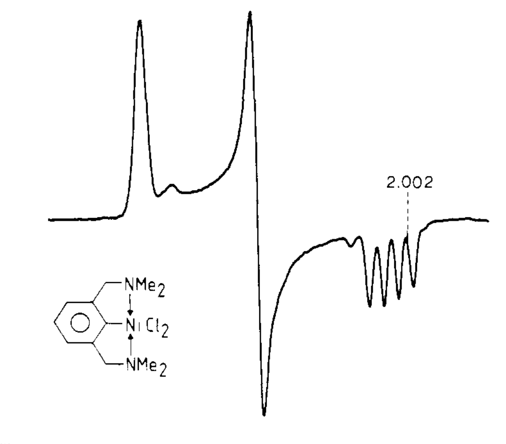


Figure 1. ESR spectrum of **1a** at –140 °C in a toluene glass.[20]

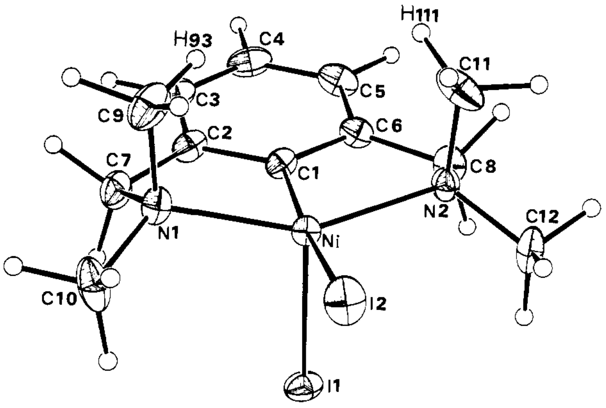


Figure 2. ORTEP drawing of Ni[$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′]I_2 (**1c**). Some relevant bond lengths (Å) and angles (deg) are as follows: Ni–I1, 2.613 (1); Ni–I2, 2.627; Ni–N1, 2.050 (4); Ni–N2, 2.038 (4); Ni–C1, 1.898 (5); N1–Ni–N2, 152.0 (2); C1–Ni–I2, 168.8 (2); I1–Ni–I2, 103.0 (1); I1–Ni–C1, 88.2 (2); I2–Ni–N1, 95.6 (1); N1–Ni–C1, 81.9 (2); I1–Ni–N1, 102.0 (1).

Some crystal data for **1c** are as follows: $C_{12}H_{19}I_2N_2Ni$, monoclinic, space group $P2_1/c$, with a = 13.9696 (9) Å, b = 7.8683 (9) Å, c = 15.0510 (17) Å, β = 108.769 (7)°, U = 1566.4 Å^3, Z = 4, D_c = 1.28 g cm^{-3}, $F(000)$ = 956 electrons, μ(Mo K$\bar{\alpha}$) = 48.6 cm^{-1}. A total of 3968 symmetry-independent reflections, from a crystal of dimensions 0.25 × 0.30 × 0.50 mm, were re-

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(1) A fairly recent review covering this subject is given in the following: Lappert, M. F.; Lednor, P. *Adv. Organomet. Chem.* **1976**, *14*, 345–399.

(2) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77–119.

(3) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87–147.

(4) The syntheses and characterization of these and related complexes will be the subject of a forthcoming publication.

(5) Complex **1b** has also been isolated in low yield from the reaction of **2b** with either Br_2 or *N*-bromosuccinimide. The copper halide reactions were carried out in acetone, whereas benzene was used for the syntheses of **1c**.

(6) An NMR method was used to measure the paramagnetism, and this gave a value of one unpaired electron per molecule at room temperature in CH_2Cl_2: Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Löliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.

(7) The UV-visible spectra of these solutions show several absorption maxima between 300 and 750 nm with ϵ values in the range 200–2000 L mol^{-1} cm^{-1}.

(8) For ESR data, complexes **1a–c** are assumed to have a principal pseudo-C_2 axis colinear with the Ni apical halide bond. $\langle g \rangle$ values for **1a–c** at room temperature are ca. 2.19, 2.17, and 2.14 respectively.

(9) Although Cl has two isotopes with $I = {}^3/_2$, it was not possible to detect their individual lines. However, Br with two isotopes (both $I = {}^3/_2$) exhibits much larger spin–spin couplings, and resolution of the separate lines is to be anticipated. This together with the second-order complications makes extraction of accurate data for **1b** and **1c** nontrivial, and further work, including measurement of Q-band spectra, is in progress.

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