aspirator, and the volatiles were distilled off to yield a white solid. To the solid was added 50 mL of dry, olefin-free pentane. The resulting suspension was stirred for a few minutes and allowed to settle, and the supernatant liquid carefully decanted via a double-ended needle to another 250-mL flask fitted as before. The remaining solid was washed with pentane (3 × 10 mL), and the pentane solutions were combined. The flask containing the alkynylborane–pentane solution was immersed in a cool water bath, and 4.2 g (60 mmol) of methyl vinyl ketone was added over 5 min. Meanwhile, 3.17 g (52 mmol) of ethanolamine was placed in a centrifuge tube. The reaction mixture was then needled into the centrifuge tube, which was cooled in an ice bath. After centrifugation to settle the precipitate, the supernatant pentane solution was transferred to a distillation setup with a 6 in. Vigreux column. The 9-BBN-ethanolamine adduct in the centrifuge tube was washed with pentane (2 × 20 mL), and the pentane solutions were combined. The pentane was evaporated and the product was distilled to provide 6.34 g (83%) of 7,7-dimethyl-5-octyn-2-one: bp 84–87 °C (20 mm); n^{20}_{D} 1.4408; IR (neat) 1720; ^{1}H NMR (CCl$_4$, Me$_4$Si) δ 1.08 (s, 9 H), 2.10 (s, 3 H), 2.20–2.75 (m, 4 H).

It is evident that this procedure makes it practical to achieve the conjugate addition of alkynyl groups to methyl vinyl ketone and related derivatives. This new 1,4-addition reaction should provide a new route to many complex molecules difficult to prepare by other means, and, moreover, marks the beginning of our studies on reactions of alkynylboranes in typical organoborane reactions.[8]

References and Notes

(1) J. A. Sinclair and H. C. Brown, *J. Org. Chem.*, **41**, 1078 (1976); *J. Organomet. Chem.*, in press.

(2) E. J. Corey and D. L. Beames, *J. Am. Chem. Soc.*, **94**, 7210 (1972).

(3) E. J. Corey and R. H. Wollenberg, *J. Am. Chem. Soc.*, **96**, 5581 (1974).

(4) J. Hooz and R. B. Layton, *J. Am. Chem. Soc.*, **93**, 7320 (1971).

(5) (a) R. Pappo and P. W. Collins, *Tetrahedron Lett.*, 2627 (1972); (b) M. Bruhn, C. H. Brown, P. W. Collins, J. R. Palmer, E. Z. Dajani, and R. Pappo, *Tetrahedron Lett.*, 235 (1976).

(6) P. Jacob, III, and H. C. Brown, *J. Am. Chem. Soc.*, **98**, 7832 (1976).

(7) R. E. Lutz and W. G. Revely, *J. Am. Chem. Soc.*, **63**, 3184 (1941).

(8) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972; H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975.

(9) Graduate research assistant on Grant MPS 73-09136 A01 from the National Science Foundation.

(10) Purdue University Fellow, 1975–1977.

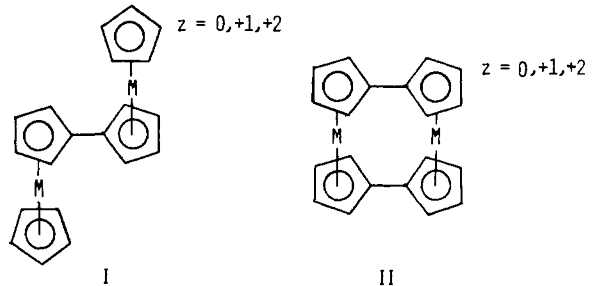
James A. Sinclair,[9] Gary A. Molander,[10] Herbert C. Brown*
Richard B. Wetherill Research Laboratory
Purdue University
West Lafayette, Indiana 47907

Received October 26, 1976

The Synthesis and Characterization of Bis(fulvalene)dinickel, in Three Oxidation Levels

Sir:

Recent interest and controversy regarding the bonding and electronic structure of iron complexes of structural type I and II[1] have led us to explore synthetic routes to other metal derivatives. We wish to report the synthesis and initial physical studies of the bis(fulvalene)dinickel system, II-Ni (z = 0, +1, +2).



I II

M = Fe, Co, Ni

The synthesis of II-Ni (z = 0) utilized an in situ preparation of the fulvalene dianion,[2] similar to that developed independently by Mueller-Westerhoff and Eilbracht for the preparation of II-Fe (z = 0),[1d,3a] and Davison and Smart for II-Co (z = +2).[3b,c] Sodium cyclopentadienide (as the crystalline mono-1,2-dimethoxyethane adduct,[3c] 9.03 g, 50.7 mmol) in THF (250 ml) at −78 °C was treated with iodine (6.7 g, 26 mmol, 5% excess) and the mixture was allowed to warm (ca. 20 min) to yield a cherry red solution of 9,10-dihydrofulvalene. This thermally unstable species[4] is formed in an oxidative coupling reaction, presumably via the intermediate formation of 5-iodocyclopentadiene[5] which undergoes nucleophilic substitution by cyclopentadienyl anion. The THF solution was immediately cooled to −78 °C, followed by the addition of *n*-butyllithium (2.4 M in hexane, 24 ml, 57.6 mmol, 14% excess) to yield a light tan solution of the fulvalene, or bicyclopentadienyl, dianion.[6]

Anhydrous nickel acetylacetonate[7] (6.84 g, 26.6 mmol, 5% excess) was added and the mixture stirred at room temperature for ca. 17 h. The resulting air-sensitive brown material was isolated by filtration, washed with deoxygenated water (200 ml) and THF (30 ml), and dried in vacuo. Extensive Soxhlet extraction of this material with mesitylene (discarding first ten extracts) yielded moderately air-sensitive, reddish brown crystalline II-Ni (z = 0) (2.83 g, 60% yield based on starting Na(DME)C$_5$H$_5$). An analytically pure sample was obtained by high vacuum sublimation at 200 °C.

Oxidation of the slightly soluble II-Ni (z = 0) with a suspension of anhydrous ferric chloride in benzene for ca. 3 days yielded a brown material that was extracted with *oxygen-saturated* dilute hydrochloric acid (pH 5) to yield an unstable orange solution of II-Ni (z = +2), which was immediately precipitated as a hexafluorophosphate salt in good yield. Recrystallization from *oxygen-saturated* acetone/ether (1/1, v/v) gave an analytically pure sample as air-stable, dark reddish brown crystals.

Orange solutions of II-Ni (z = +2) are somewhat unstable towards reduction to the purple mixed-valence derivative II-Ni (z = +1). This derivative was isolated as an analytically pure, air-stable, very dark purple microcrystalline hexafluorophosphate salt by warming pure II-Ni (z = +2) in acetonitrile, followed by crystallization from acetonitrile/ethanol. Alternatively, this compound was prepared from II-Ni (z = 0), by oxidation with 1 equiv of ferrocinium hexafluorophosphate in THF at 25 °C for 2 h. Methathesis reactions have yielded B(C$_6$H$_5$)$_4^-$, BF$_4^-$, and I$_3^-$ salts.

Previous physical studies[1a–c] indicate that biferrocene derivatives, I-Fe (z = 0, +1, +2), can be viewed qualitatively as substituted ferrocenes or ferrocinium ions, with integral oxidation states of iron. The mixed-valence I-Fe (z = +1) exhibits a unique near-infrared absorbance at 1800 nm (ϵ 750) that has been assigned[1a] as an intervalence transfer transition from theory developed by Hush[8] and utilized by Day.[9] The mixed-valence II-Fe (z = +1) also exhibits unique infrared bands centered at 1550 nm (ϵ 2100) that are absent in both the z = 0, +2 oxidation levels, as well as in ferrocene and the ferrocinium ion. However, the applicability of the Hush model in assigning these transitions has been questioned, and controversy has developed as to whether the II-Fe system (z = 0, +1, +2) exhibits rapid intervalence electron transfer via direct metal-metal exchange,[1c] or is a completely delocalized system involving a ligand-propogated exchange.[1d]

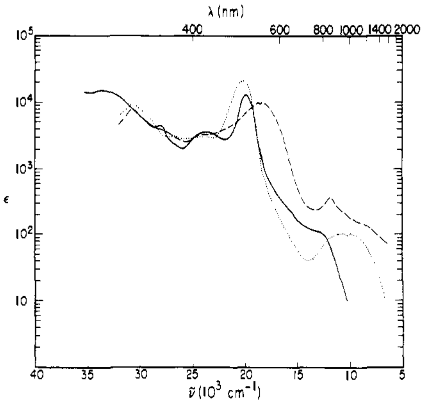


Figure 1. Electronic absorption spectra of bis(fulvalene)dinickel, II-Ni (z = 0) (—) in benzene; (z = +1) (- - -) and (z = +2) (· · ·) as hexafluorophosphate salts in acetone.

We have found that both II-Co (z = 0, +1) exhibit very similar infrared absorbances at 980 nm (ε 1150 and 7000, respectively), with shoulders at lower energy. These bands are absent in cobaltocene and the cobalticinium ion. The electronic spectra of the II-Ni system in Figure 1 indicate the presence of somewhat similar near-infrared absorbances for the three oxidation levels thus far isolated. These bands are absent in the "parent" nickelocene[11] and nickelocinium ion.[10] *Although these bands are the most intense in the mixed-valence derivative of cobalt and nickel, the presence of seemingly analogous near-infrared bands in other derivatives suggests that they are not intervalence transfer transitions associated with electron transfer from one localized metal center to another.*

Magnetic susceptibility measurements of solid samples of II-Fe,[1c,d] Co,[10] Ni[12] (z = 0, +2) show them to be diamagnetic at room temperature. The mixed-valence II-Co,[3c] Ni (z = +1) have $S = \frac{1}{2}$ ground states with magnetic moments close to that of the free electron value. The susceptibility of II-Ni (z = +1) tetraphenylborate follows Curie law from 3.5 to 82.0 K with $\mu_{\text{eff}} = 1.79\ \mu_B$. A $\mu_{\text{eff}} = 1.7\ \mu_B$ at 300 K was found for the hexafluorophosphate salt by the Evans NMR method.[13] These results indicate that complete magnetic coupling is facilitated in the bis(fulvalene)dimetal system containing from 34 to 40 valence electrons. To what degree this coupling is the result of direct metal-metal exchange or is propagated by the bridging ligands remains to be determined. However, a comparison of ultraviolet and visible spectra indicates that there are qualitative differences among the different oxidation levels of the cobalt and nickel complexes, as well as their "parent" metallocenes. These observations suggest that the bis(fulvalene) dimetal systems have electronic structures that are distinctly different from metallocenes.

Further evidence for geometric and electronic structural differences in these compounds is provided by a comparison of their infrared spectra. A variation in the number of bands in the carbon-carbon stretching region, as well as distinct differences in the lower energy region, is observed for each oxidation level of both II-Co, Ni, systems. These observations suggest that a ligand propogated exchange is occurring in bis(fulvalene)dimetal complexes containing more than 36 valence electrons, with concurrent changes occurring in the ligand geometry. A complete understanding of the structure and bonding of this interesting class of compounds will require further physical and structural studies, and will be aided by the synthesis of other bis(fulvalene)dimetal and bimetallocene derivatives.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Energy Research and Development Administration for support of this research. The technical assistance of Mr. V. Tashinian and Ms. Sheri Ogden is also gratefully acknowledged.

References and Notes

(1) (a) D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, **6,** 1 (1973); (b) C. LeVanda, D. O. Cowan, and K. Bechgaard, *J. Am. Chem. Soc.*, **97,** 1980 (1975); (c) W. H. Morrison, Jr., and D. H. Hendrickson, *Inorg. Chem.* **14,** 2331 (1975); (d) C. LeVanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candella, and R. L. Collins, *J. Am. Chem. Soc.*, **98,** 3181 (1976).
(2) (a) W. v. E. Doering, "Theoretical Organic Organic Chemistry, The Kekule Symposium", Butterworths, London, 1959; (b) E. A. Matzner, Ph.D. Thesis, Yale University, 1958.
(3) (a) U. Mueller-Westerhoff and P. Eilbracht, *J. Am. Chem. Soc.*, **94,** 9272 (1972); (b) A. Davison and J. C. Smart, *J. Organomet. Chem.*, **49,** C43 (1973) (c) J. C. Smart, Ph.D. Thesis, MIT, 1973.
(4) (a) E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Am. Chem. Soc.*, **90,** 5284 (1968); (b) D. W. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropulos, and E. Hedaya, *J. Am. Chem. Soc.*, **96,** 4673 (1974).
(5) R. Breslow and J. Hoffman, *J. Am. Chem. Soc.*, **94,** 2110 (1972).
(6) All manipulations must be performed with the rigorous exclusion of air to obtain a light colored solution and good yields.
(7) R. G. Charles and M. A. Paulikowski, *J. Chem. Phys.*, **62,** 440 (1958). $Ni(acac)_2$ was sublimed prior to use.
(8) N. S. Hush, *Prog. Inorg. Chem.*, **8,** 391 (1967).
(9) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10,** 247 (1967).
(10) J. C. Smart and B. Pinsky, unpublished results.
(11) R. D. Scott and R. S. Becker, *J. Chem. Phys.*, **35,** 516 (1961).
(12) Analytically pure samples of II-Ni (z = 0) exhibited varying small amounts of paramagnetisim. Careful inspection of the mass spectra of different samples indicated the presence of differing small amounts of a $C_{20}H_{18}Ni_2^+$ ion within the parent peak envelope of the $C_{20}H_{16}Ni_2^+$ ion. This may indicate the presence of trace amounts of binickelocene, as was found for analogous compounds in the iron[3a] and cobalt[3b] preparations, or partially hydrogenated material formed under the extraction conditions. Diamagnetic samples of II-Ni (z = 0) were prepared by reduction of pure samples of II-Ni (z = +1, +2) with sodium dispersion.
(13) D. H. Evans, *J. Chem. Soc.*, 2003 (1959).

James C. Smart,* Barry L. Pinsky
Department of Chemistry and Materials and Molecular
Research Division of the Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Received September 28, 1976

Prenyltransferase. New Evidence for an Ionization-Condensation-Elimination Mechanism with 2-Fluorogeranyl Pyrophosphate[1]

Sir:

The mechanism of the head-to-tail condensation between isopentenyl pyrophosphate (IPP) and an allylic pyrophosphate catalyzed by prenyltransferase (EC 2.5.1.1) has been the subject of speculation since the biosynthetic pathway was first uncovered over 20 years ago.[2] The earliest proposals envisioned carbon-carbon bond formation between C(4) of isopentenyl pyrophosphate and C(1) of the allylic substrate via cationic intermediates.[3] About ten years ago the ionization-condensation-elimination mechanism was replaced by the "X-group" mechanism (a displacement-elimination sequence), which was thought to be more compatible with the stereochemistry of the prenyltransfer reaction.[4] After examining the data which had been published we decided that it was not possible to distinguish between the two mechanisms. Although the stereochemistry of the enzyme-catalyzed reaction is compatible with that of the individual steps of the displacement-elimination mechanism,[4c] it is quite possible that the stereospecificity found for the reaction is dictated by the topology of the active site of prenyltransferase.[5]

We reasoned that it would be possible to distinguish between the two mechanisms by selectively substituting hydrogen with fluorine in the allylic substrate. The powerful electron withdrawing effect of fluorine should retard ionization of the allylic pyrophosphate, while having little influence on the rate of a direct nucleophilic displacement.[6] We recently reported that