99, 2802 (1977).

(4) M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, in press.

(5) M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 531 (1977).

(6) R. B. King and K.-N. Chen, *Inorg. Chim. Acta*, **23**, L19 (1977).

(7) J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, **13**, 363 (1970).

(8) The compounds [C$_5$H$_5$FeCO]$_2$(PF$_2$)$_2$NCH$_3$ and [C$_5$H$_5$Fe(PF$_2$)$_2$NCH$_3$]$_2$ were characterized by correct C, H, N, P, and F analyses and correct molecular weight determinations in benzene solution by vapor pressure osmometry.

(9) R. J. Haines and A. L. Du Preez, *J. Organomet. Chem.*, **21**, 181 (1970).

(10) University of Georgia Graduate Fellow, 1976–1978.

(11) Permanent address: Departmento de Quimica Inorganica, Universidad de Zaragoza, Spain.

M. G. Newton, R. B. King, M. Chang,[10] J. Gimeno[11]

*Department of Chemistry, University of Georgia
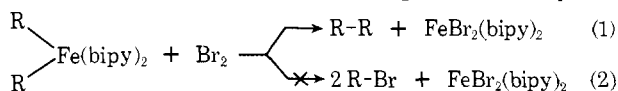Athens, Georgia 30602*

Received November 14, 1977

Reductive Coupling of Organometals Induced by Oxidation. Detection of Metastable Paramagnetic Intermediates

Sir:

The labilization of organometal intermediates is vital to the success of many catalytic organic processes. Indeed, a large number and variety of rather stable alkyl derivatives of transition metals are now known,[1] and it is necessary to find factors which determine how the alkyl–metal bond is selectively cleaved.
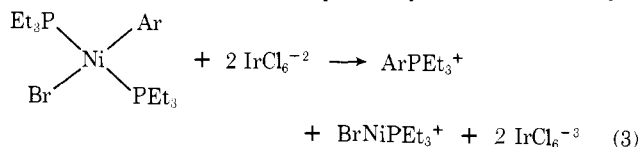
We wish to show that otherwise stable organometal complexes can be induced to undergo facile reductive coupling of a pair of alkyl ligands when subjected to oxidation. For example, dialkyl(bipyridyl)iron(II) complexes, $R_2Fe(bipy)_2$, usually afford a mixture of hydrocarbons consisting mostly of disproportionation products (RH and R(-H)) on thermolysis.[2] However, these six-coordinate complexes decompose immediately at room temperature when treated with a variety of reagents listed in Table I, especially the 1-equiv oxidants such as hexachloroiridate(IV) and cerium(IV). The most striking result is the high yields of coupled products, R–R, obtained with even halogens.[3] Reductive coupling of alkyl groups in-

$$R \diagdown \atop R \diagup Fe(bipy)_2 + Br_2 \longrightarrow \Big\{ \begin{array}{l} R-R + FeBr_2(bipy)_2 \quad (1) \\ 2\,R-Br + FeBr_2(bipy)_2 \quad (2) \end{array}$$

duced in this manner appears to be intramolecular, since no crossover product (propane) is obtained when mixtures of methyl- and ethyliron derivatives are treated. Similar results are obtained with the other transition metal analogues,

$(CH_3)_2Co(acac)(PMe_2Ph)_2$ and $(CH_3CH_2)_2Co(acac)(PMe_2Ph)_2$.[4]
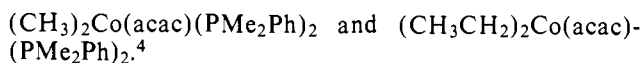
Cis and trans, square-planar organonickel(II) complexes also undergo reductive coupling under similar conditions. Thus, *n*-butane is the major product from *cis*-diethyl(bipyridine)-nickel(II), $(CH_3CH_2)_2Ni(bipy)$, when it is treated with either Na_2IrCl_6, Br_2, or even O_2 in THF solutions.[5] Similarly, the thermally stable diarylnickel(II) complexes, *trans*-Ar$_2$Ni-(PEt$_3$)$_2$, afford excellent yields of biaryls when treated with either Na_2IrCl_6, $CuBr_2$, Br_2, I_2, ICl, Co(III), Ce(IV), or Tl(III) trifluoroacetates.[6] Reductive coupling of ligands is not limited to only metal complexes containing two carbon-centered ligands. When a series of stable monoarylnickel(II) complexes, *trans*-ArNi(X)(PEt$_3$)$_2$, were treated with these reagents, arylphosphonium salts containing ArPEt$_3^+$ were formed in excellent yields, with X = Br, Cl, I, NCS, NO$_2$, and NCO.[7] The arylphosphonium group is also readily eliminated from *trans*-ArNi(X)(PEt$_3$)$_2$ with hexachloroiridate, when X = CN and CH$_3$, but it is accompanied by ArCN and ArCH$_3$.[7b]

$$\begin{array}{c} Et_3P \diagdown \atop Br \diagup Ni \diagdown \atop \diagup PEt_3 \end{array} \begin{array}{c} Ar \end{array} + 2\,IrCl_6^{-2} \longrightarrow ArPEt_3^+$$

$$+ BrNiPEt_3^+ + 2\,IrCl_6^{-3} \quad (3)$$

The stoichiometry of arylphosphonium elimination induced by hexachloroiridate is represented by eq 3. If the reaction of *o*-CH$_3$C$_6$H$_4$NiBr(PEt$_3$)$_2$ is carried out at -50 °C, an intense, stable electronic spectrum with λ_{max} 410 nm and ESR spectrum with $g = 2.196$ are observed immediately, independent of whether Na_2IrCl_6, Ce(TFA)$_4$, or CuBr$_2$ is employed. The g value, however, varies with the aryl group, being shifted to 2.205 and 2.198 with Ar = *o*-CH$_3$OC$_6$H$_4$ and *o*-ClC$_6$H$_4$, respectively. We ascribe these spectral changes to a paramagnetic nickel(III) species[8] formed by 1-equiv oxidation.[9]

$$ArNiBr(PEt_3)_2 + IrCl_6^{-2} \to ArNiBr(PEt_3)_2^+ + IrCl_6^{-3} \quad (4)$$
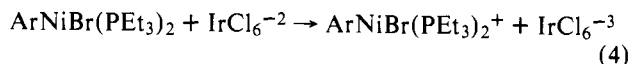
On warming this solution to -18 °C, the ESR spectrum disappeared irreversibly with a half-life of $\sim$20 min, which we associate with reductive elimination from the paramagnetic arylnickel(III) species.[10]

$$ArNiBr(PEt_3)_2^+ \to ArPEt_3^+ + BrNiPEt_3 \quad (5)$$

Independent experiments show that similar nickel(I) complexes[11] are readily converted to nickel(II) derivatives under the conditions of these experiments.

The oxidation of ArNiBr(PEt$_3$)$_2$ in eq 4 does not go to completion, since more than an equivalent amount of Na$_2$IrCl$_6$ is required to convert it completely to the paramagnetic nick-
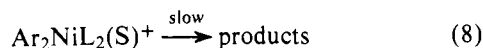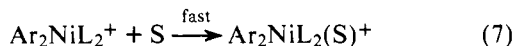
Table I. Induced Decomposition of Dialkyliron(II) Complexes[a]

Me$_2$Fe(bipy)$_2$,[b] mmol	Et$_2$Fe(bipy)$_2$, mmol	Reagent	Products, mmol				
			MeH	Me–Me	Me–Et	Et–Et	Other
0.05		Na$_2$IrCl$_6$	0.007	0.034			c, d
0.05		Br$_2$	0.002	0.030			e
	0.05	Na$_2$IrCl$_6$		0.005		0.044	c
	0.05	Br$_2$		0.002		0.048	
0.05	0.05	Na$_2$IrCl$_6$	0.009	0.040	0	0.051	c, f
0.05	0.05	Br$_2$	0.002	0.030	0	0.051	g
	0.05	Cl$_2$		0.005		0.046	c
	0.05	I$_2$		0.002		0.031	c
	0.05	ICl		0.002		0.043	
	0.05	Tl(TFA)$_3$		0.002		0.052	c
	0.05	Ce(TFA)$_4$		0.007		0.050	c
	0.05	Co(OAc)$_3$		0.003		0.053	c

[a] In 3 mL of THF at 25 °C with excess reagent under argon. All reactions occurred on mixing. [b] This compound is difficult to purify and may be slightly impure. [c] Traces (<0.001 mmol) of ethylene detected. [d] No methyl chloride. [e] Methyl bromide (0.011 mmol). [f] No methyl or ethyl chloride. [g] Methyl and ethyl bromides (0.014 and 0.006 mmol).

el(III) species using an ESR probe. Moreover, an equilibrium constant of $\sim 10^{-2}$ is deduced by measuring the intensity of the hexachloroiridate absorption with stop-flow techniques in the presence of varying amounts of o-$CH_3C_6H_4NiBr(PEt_3)_2$. Quenching the paramagnetic species at $-50\,^\circ C$ with zinc dust leads to about 50% recovery of the reactant.

A preliminary electrochemical study of $Ar_2Ni(PEt_3)_2$ was examined at a stationary platinum electrode in acetone solution by cyclic voltammetry. A single anodic peak P_1 was observed at 0.68 V relative to SCE.[12] The reverse scan exhibited a single cathodic peak P_2 at -0.38 V which is associated with the oxidation observed at P_1. If the scan is restricted to voltages <0.5 V, the reduction at P_2 is not observed. Therefore, P_2 cannot be due to a primary reduction of Ar_2NiL_2. The oxidation of Ar_2NiL_2 is irreversible at all scan rates even at $-78\,^\circ C$. However, the current ratio $I_p^{(2)}/I_p^{(1)}$ is independent of the scan rate, and its magnitude, 0.53, though less than the ideal limit of 1.0, is quite large. Thus, P_2 is attributable to the reduction of a major intermediate in the oxidation of Ar_2NiL_2. Furthermore, the lifetime of this intermediate must be comparable with the time scale of the electrochemical measurement. We tentatively propose the following EC mechanism,[13] in which the cathodic process P_2 corresponds to the reduction of the solvated intermediate, $Ar_2NiL_2(S)^+$.

$$Ar_2NiL_2 \xrightarrow{-\epsilon} Ar_2NiL_2^+ \qquad (6)$$

$$Ar_2NiL_2^+ + S \xrightarrow{fast} Ar_2NiL_2(S)^+ \qquad (7)$$

$$Ar_2NiL_2(S)^+ \xrightarrow{slow} products \qquad (8)$$

where $L = PEt_3$, Ar, o-$CH_3OC_6H_4$ and $S =$ solvent.

The substitution-lability of the paramagnetic nickel(III) species in eq 7[14] is also shown in the ready addition of carbon monoxide at $-50\,^\circ C$ to afford the acylnickel(III) species ($g = 2.16$)

$$ArNiBr(PEt_3)_2^+$$
$$\xrightarrow{CO} ArCONiBr(PEt_3)_2^+ \xleftarrow{-\epsilon} ArCONiBr(PEt_3)_2$$
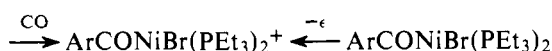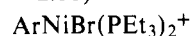
which is identical with that obtained independently by oxidation of the acylnickel(II) complex[15] with Na_2IrCl_6.[16] A paramagnetic nickel(III) species can also be obtained from bromine oxidation of $ArNiBr(PEt_3)_2$. Although it is different from that obtained with Na_2IrCl_6, having a g value of 2.194 and undergoing a more rapid reductive elimination, it can be converted to the same acylnickel(III) species if phosphine is added in the presence of CO. The pattern of reactivity of halogen toward organometals is similar to that observed in Table I with 1-equiv oxidants. The labilization of alkyl–metal bonds under these conditions has bearing on the mechanism of electrophilic cleavage of transition metal bonds generally, especially in the light of oxidative processes already identified in some cases.[17]

References and Notes

(1) (a) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976); (b) R. R. Schrock and G. W. Parshall, *ibid.*, **76**, 243 (1976).
(2) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Am. Chem. Soc.*, **90**, 1878 (1968); T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **45**, 1104 (1972).
(3) (a) The formation of butane when $Et_2Fe(bipy)_2$ was treated with I_2 was originally noted by Yamamoto and coworkers.[2] (b) The iron-containing product was inferred from the iodonolysis results.[2] Further characterization is in progress.
(4) (a) For preparation and thermolysis, see T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, **120**, 257 (1976). (b) From 0.043 mmol of Me_2Co^{III} complex, 0.043 mmol of ethane with Na_2IrCl_6 and 0.038 mmol of C_2H_6, 0.004 mmol of CH_4, and 0.006 mmol of CH_3Br with Br_2. The diethyl derivative gives analogous results but is complicated by facile phosphine dis-

sociation as described by T. Ikariya, Y. Nakamura, and A. Yamamoto, *ibid.*, **118**, 101 (1976).
(5) From 0.050 mmol of $Et_2Ni(bipy)$, the formation of n-butane, ethane, and ethylene was 0.024, 0.007, <0.001 mmol from Na_2IrCl_6, 0.025, 0.003, 0 mmol from Br_2, and 0.018, 0.009, and 0.011 mmol from O_2. In addition, 0.034 mmol of EtBr was observed with Br_2.
(6) The yields of di-o-anisyl from 0.070 mmol of $(o$-$CH_3OC_6H_4)_2Ni(PEt_3)_2$ was 0.064, 0.063, 0.051, 0.023, 0.038, and 0.043 mmol from $Co(TFA)_3$, $Ce(TFA)_4$, $Tl(TFA)_3$, $CuBr_2$, Na_2IrCl_6, and Br_2, respectively. In addition, $CuBr_2$ produced 0.013 mmol of o-anisyl bromide and $NaIrCl_6$ produced 0.076 mmol of o-anisyltriethylphosphonium ion.
(7) (a) From o-$CH_3OC_6H_4NiBr(PEt_3)_2$ the yields of o-$CH_3OC_6H_4PEt_3^+$ were 86, 100, 76, 69, 76, 49, and 0% from $K_3Fe(CN)_6$, $Tl(TFA)_3$, $Co(TFA)_3$, $Ce(TFA)_4$, $CuBr_2$, and $Hg(TFA)_2$, respectively. (b) The treatment of o-$CH_3C_6H_4NiX(PEt_3)_2$ with Na_2IrCl_6 afforded o-$CH_3C_6H_4PEt_3^+$ in 89, 80, 78, 82, 52, and 80% yields for X = Cl, Br, I, NO_2, CN, and CH_3. In addition, 42% o-tolunitrile and 13% o-xylene were obtained for X = CN and CH_3, respectively.
(8) For nickel(III) complexes, see G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965); D. W. Meek, E. C. Alyea, J. K. Stalick, and J. A. Ibers, *J. Am. Chem. Soc.*, **91**, 4920 (1969); A. Wolberg and J. Manassen, *Inorg. Chem.*, **9**, 2365 (1970); R. S. Drago and E. I. Baucom, *ibid.*, **11**, 2064 (1972); J. G. Mohanty and A. Chakravorty, *ibid.*, **15**, 2912 (1976).
(9) The 1-equiv oxidation of other alkylmetals by hexachloroiridate(IV) has been established with alkylcobalt(III),[9a] alkylplatinum(II),[9b] alkylmercury(II),[9c] and alkyllead(IV):[9d] (a) J. Halpern and J. Topich, *Inorg. Chim. Acta*, **20**, L21 (1976); S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972); (b) J. Y. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, **99**, 1450 (1977); (c) J. Y. Chen, H. C. Gardner and J. K. Kochi, *ibid.*, **98**, 6150 (1976); (d) H. C. Gardner and J. K. Kochi, *ibid.*, **97**, 1855 (1975).
(10) (a) Paramagnetic intermediates may also be involved in the reductive coupling accompanying the oxidation of other organometals such as alkylcopper(I) (G. M. Whitesides, J. San Filippo, Jr., C. P. Casey, and E. J. Panek, *J. Am. Chem. Soc.*, **89**, 5302 (1967); **91**, 4871 (1969)), arylnickel(II) (D. Morrell and J. K. Kochi, *ibid.*, **97**, 7262 (1975)), acylmanganese(I) (C. P. Casey and C. A. Bunnell, *ibid.*, **98**, 436 (1976)), and alkylgold(I,III) (S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *ibid.*, **99**, 8440 (1977)). (b) Homolysis of the paramagnetic intermediate to afford alkyl radicals is also known (see ref 9b–d; for $(CH_3)_2Co(DO)(DOH)pn$, W. T. Tamblyn, unpublished results).
(11) For nickel(I) complexes, see D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, *Can. J. Chem.*, **52**, 2990 (1974); M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, **12**, 167 (1975); L. Porri, M. C. Gallazzi, and G. Vitulli, *Chem. Commun.*, 228 (1967). Cf. also M. J. Nilges, E. K. Barefield, R. L. Belford, and P. H. Davis, *J. Am. Chem. Soc.*, **99**, 755 (1977).
(12) The current function $I_p/v^{1/2}C$ for P_1 is independent of the scan rate, v, and is less than that observed for the known one-electron oxidation of ferrocene.
(13) (a) Compare a similar electrochemical behavior with the dicyanonickel(II) analogue, *trans*-$(NC)_2Ni(PEt_2Ph)_2$: G. Bontempelli, C. Benedetto, and F. Magno, *Anal. Chem.*, **49**, 1005 (1977). (b) Low temperature coulometry at controlled potentials will be examined.
(14) The rapid solvation of the paramagnetic nickel(III) intermediate in eq 7 suggests that this species prefers to be five coordinate. Indeed, in an analogous situation, the rhodium(III) complexes, $(bipy)_2RhCl_2^+$ and $(bipy)_3Rh^{+3}$, upon reduction both rapidly lose one ligand to form the five-coordinate rhodium(II) intermediates, $(bipy)_2RhCl^+$ and $(bipy)_2Rh(S)^+$, respectively: G. Kew, K. DeArmond, and K. Hanck, *J. Phys. Chem.*, **78**, 727 (1974).
(15) Cf. H. F. Klein, *Angew. Chem. Int. Ed. Engl.*, **12**, 402 (1973).
(16) The variation in yields of coupled products with oxidants (cf. Table I and notes 5, 6, and 7) suggest that the fates of the paramagnetic intermediates may depend on such anation.
(17) (a) For a recent review, see G. W. Daub, *Prog. Inorg. Chem.*, **22**, 409 (1977). (b) Cf. also V. V. Lalaev and A. P. Belov, *Zh. Obsch. Khim.*, **46**, 2753 (1976).

T. T. Tsou, J. K. Kochi*
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received November 15, 1977

Manifestations of Sulfur to Sulfur Through-Space Interactions in Complex Ion Spectra

Sir:

Musker and coworkers[1,2] have described some remarkable redox characteristics of 1,5-dithiocane. The structural features that facilitate the oxidation of the molecule to a monopositive and to a dipositive ion lead to some rather unexpected effects when the molecule is a ligand, which we report in this paper. A splitting of the ligand to metal charge-transfer band in the visible is observed when the ligand is coordinated to Ru(III); furthermore, a strong intervalence absorption is observed in the Ru(III)–Ru(II) mixed valence complex despite the fact