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Facile cleavage of a C–C bond in a dinuclear nickel complex

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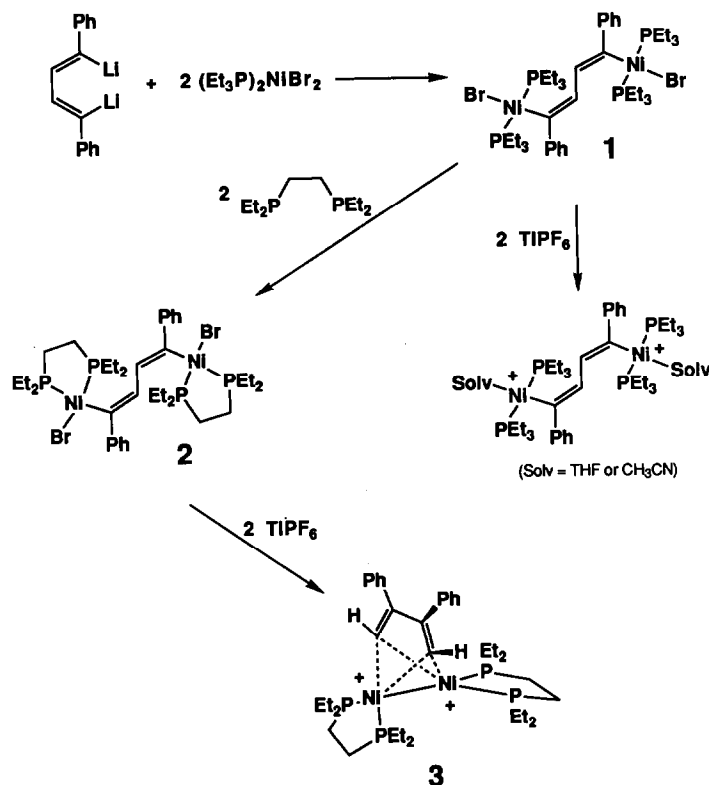
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Abstract

Facile C–C cleavage is demonstrated to occur upon treatment of $\{(depe)NiBr\}_2(\mu-Z, Z-PhC=CH-CH=CPh)$ with $TiPF_6$. The implications of this reaction for the Reppe cyclotramerization of alkynes are discussed.

Dinuclear complex **1** (see Scheme 1) has been prepared in 80% yield by reaction of (*E,E*)-1,4-dithio-1,4-diphenylbutadiene with $(Et_3P)_2NiBr_2$ in a 1 : 2 molar ratio [1]. Reaction of **1** with two equivalents of $TiPF_6$ in the presence of THF or acetonitrile results simply in replacement of the bromine on each nickel by a solvent molecule to give a dicationic product from which **1** can be regenerated by treatment with sodium bromide. In surprising contrast, the major product from reaction of **2** with two equivalents of $TiPF_6$ (the best yield so far, 78%, comes from using nitromethane solvent at room temperature, overnight) is complex **3**, identified by X-ray crystallography (see Fig. 1) [2*]. The presence of hydrogens on C2 and C2a cannot be deduced rigorously from the crystal structure but can from the 1H NMR spectrum which at 200 MHz in acetone- d_6 shows δ 8.65 (quintet, 2H), 7.47 (m, 10H), 2.5–1.7 (m, 24H), 1.31 (m, 12H), 0.92 (m, 12H). The multiplicity of the resonance corresponding to the hydrogens on C2 and C2a (δ 8.65) requires some comment: apparently (and not surprisingly) the small deviation from C_{2v} symmetry seen in the X-ray structure is not observed in the NMR spectrum. Even for C_{2v} symmetry, though, each of the observed hydrogens should experience coupling to two magnetically inequivalent sets of phosphorus nuclei, leading to a nine-line pattern. The observation of only a five-line resonance could imply some kind of dynamic process that renders all four phosphorus nuclei equivalent, but we believe that this is not the case; the second and fourth lines of the multiplet are broader than the first, third, and fifth. Such a spectrum can be explained by coupling constants that are close but not identical to the two sets of phosphorus nuclei. In fact the positions and relative widths of the lines can be simulated with $J(PH) = 8.6$

* Reference number with asterisk indicates a note in the list of references.



Scheme 1.

Hz and $J(\text{P}'\text{H}) = 7.4$ Hz. Also arguing against a dynamic process is the ^{13}C NMR spectrum (100.58 MHz, acetone- d_6), which shows what appears to be a symmetrical nine-line resonance at δ 164.3 for C2 and C2a, overlapped by a singlet (presumably due to C1 and C1a) at δ 164.6. The FAB mass spectrum of the bis(hexafluorophosphate) salt of **3** shows peaks at 879 (21.6%), 878 (10.3%), and 877 (24.9%) for the mono(hexafluorophosphate) cation.

The striking feature of **3** is the rearrangement that has occurred in the butadienediyl ligand. Such a reorganization appears to require cleavage of the C2–C3 bond of the original hydrocarbon ligand [**3***]. This is rather surprising because the C2–C3 bond of a 1,3-diene is very strong, in fact even stronger than that of an alkane (112 vs. 88 kcal/mol) [4]. While metal insertions into strong bonds are now quite common (C–H activation, for example), these processes usually derive their thermodynamic driving force from a change in oxidation state of the metal. In the present case no change of oxidation state has occurred.

A plausible mechanism for the reaction leading to **3** would be fragmentation to two Ni^{I} phenylacetylene complexes followed by dimerization to **3** [**5***]. If this indeed the mechanism, then the mononuclear fragments must recombine faster than they can diffuse out of the solvent cage, because a double-labeling crossover experiment, in which **2** was mixed with an equal quantity of an analogue in which the two phenyl rings were perdeuteriated, resulted in the formation of only d_0 and d_{10} products as judged by FAB mass spectrometry. Alternative intramolecular

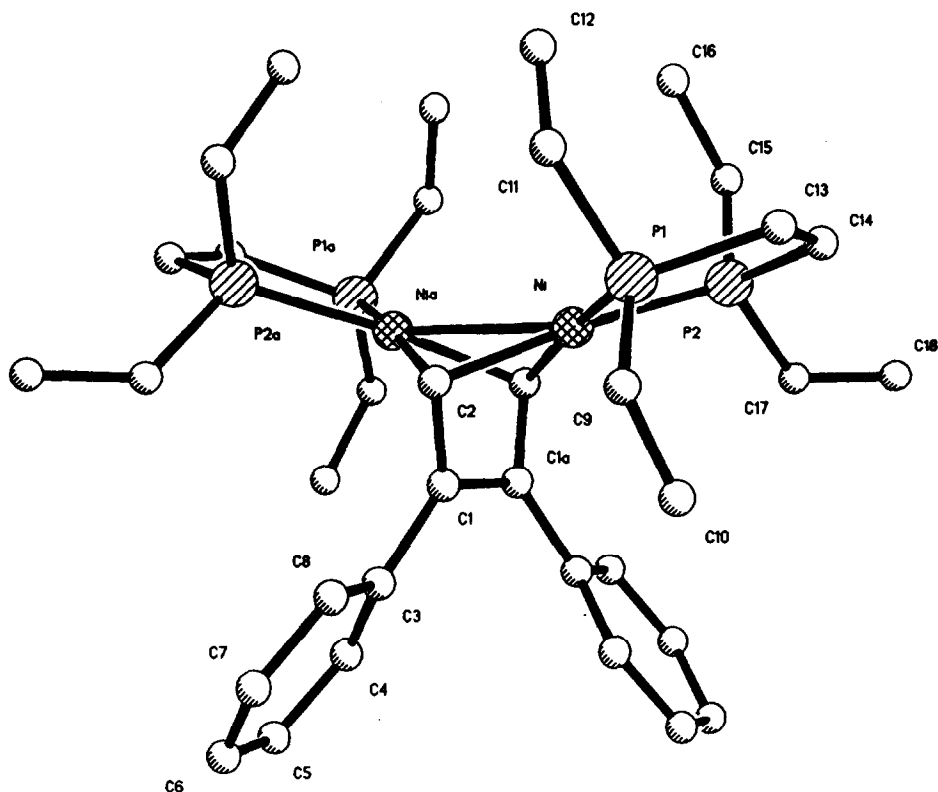


Fig. 1. Computer-generated perspective diagram of complex 3. Selected bond lengths (\AA) and angles (deg) are as follows: Ni–Nia, 2.565(2); Ni–C2, 1.912(8); Nia–C2, 1.987(7); C1–C2, 1.382(11); C1–C1a, 1.489(17); C1–C3, 1.478(11); Ni–C2–Nia, 82.3(3); C2–Ni–C2a, 83.3(4); Ni–C2–C1, 97.9(5); C3–C1–C1a, 123.9(5); C2–C1–C3, 123.8(7); C1a–C1–C2, 112.1(5).

mechanisms involving a diphenylcyclobutadiene or other cyclic intermediate are possible but poorly precedented.

It is not yet known whether the unsaturated nature of the ligand provides special kinetic facility to the σ bond cleavage (despite the very significant strengthening of the C–C bond accompanying the unsaturation, as mentioned above). It is also not known why the reaction appears to require a vacant *cis* coordination site, as judged by the contrasting behavior of 1 and 2. These questions are currently under investigation.

It is interesting to note that the rearrangement of 2 to 3 converts a 1,4-diphenylbutadienyl ligand into a 2,3-diphenylbutadienyl ligand. It is possible that such rearrangements play a role in the catalytic cyclotrimerization and cyclotetramerization of phenyl acetylene with nickel, since the major (virtually exclusive) cyclotrimer and cyclotetramer formed in this reaction (1,2,4-triphenylbenzene and 1,3,5,8-tetraphenylcyclooctatetraene, respectively) each display vicinal diphenyl substitution. This hypothesis is supported by the observation that treatment of (depe)NiBr₂ with (*E,E*)-1,4-dilithio-1,4-diphenylbutadiene results in the formation of the cyclotrimer and cyclotetramer observed in the catalytic reaction. This stoichiometric reaction cannot occur without C–C cleavage and recombination [1].

References and notes

- 1 C.J. Lawrie, K.P. Gable and B.K. Carpenter, *Organometallics*, 8 (1989) 2274.
- 2 Crystal data for **3**: $C_{36}H_{60}F_{12}P_6Ni_2$, $M = 1024.10$, monoclinic, space group $C2/c$, a 12.157(4), b 19.021(4), c 21.782(7) Å, U 4839(2) Å³, $F(000) = 1060$, $Z = 8$, $R = 0.0727$ for 2465 reflections with $F/\sigma(F) > 4.0$.
- 3 There is the *formal* possibility that the reaction took place by a four-way exchange of hydrogen and phenyl substituents on an intact butadienediyl skeleton, but such a reaction is without precedent. It, too, would require a facile C–C cleavage, now between the skeleton and the phenyl substituents. A referee has raised the possibility that, if the product is considered to be a cyclobutene complex, no C–C cleavage need be invoked, but, aside from the fact that such a σ -coordinated hydrocarbon would be unprecedented, the C2–C2a distance is 2.529 Å which does not permit any significant C–C bonding.
- 4 S.W. Benson, *Thermochemical Kinetics*, 2nd ed., Wiley Interscience, New York, 1976, p. 309. See also W. von E. Doering, *Proc. Natl. Acad. Sci. USA*, 78 (1981) 5279, for corrections to the alkyl radical data.
- 5 Such a dimerization is known for Ni^0 to give a neutral complex with a geometry whose similarity to that of **3** is remarkable given the difference in oxidation state. (R. Diercks, L. Stamp, J. Kopf and H. tom Dieck, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 893). A related structure has also been reported recently (W. Bonrath, S. Michaelis, K.R. Pörschke, B. Gabor, R. Mynott and C. Krüger, *J. Organomet. Chem.*, 397 (1990) 255).