

Carbon–Carbon Bond Cleavages in Agostic Cations Formed by Protonation of Cobalt–Diene Complexes

Martin A. Bennett,^{a*} Julian C. Nicholls,^b A. K. Fazlur Rahman,^a Alan D. Redhouse,^b John L. Spencer,^{*b} and Anthony C. Willis^a

^a Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

^b Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

The fluxional, agostic, norborn-5-en-2-ylcobalt(III) cations $[\text{Co}(\eta\text{-C}_5\text{R}_5)(2:5,6\text{-}\eta\text{-C}_7\text{H}_9)]^+$ ($\text{R} = \text{H}, \text{Me}$) undergo C–C bond cleavage at -20°C to give 4-vinylcyclopentenylcobalt(III) complexes $[\text{Co}(\eta\text{-C}_5\text{R}_5)(1\text{-}3:6,7\text{-}\eta\text{-CH}_2\text{=CHCH}(\text{CH})_3\text{CH}_2)]^+$ [$\text{R} = \text{H}$ (**4**) (structurally characterized by X-ray crystallography), Me (**7**)], which react with LiAlH_4 or LiBHET_3 to give neutral 4-vinylcyclopentenecobalt(I) complexes $[\text{Co}(\eta\text{-C}_5\text{R}_5)(1,2:6,7\text{-}\eta\text{-CH}_2\text{=CHCH}_2\text{CH=CHCH}_2)]$ [$\text{R} = \text{H}$ (**8**), Me (**9a**)]; (**9a**) is protonated at 0°C to give the 4-ethylcyclopentenyl complex $[\text{Co}(\eta\text{-C}_5\text{Me}_5)\{1\text{-}3\text{-}\eta\text{-C}_5\text{H}_6(\textit{endo}\text{-Et-}4)\}]^+$ (**11**), which is stabilized by an agostic interaction between cobalt and the *endo*-hydrogen–carbon bond of the 5-position, and readily undergoes conrotatory ring-opening to afford $[\text{Co}(\eta\text{-C}_5\text{Me}_5)\{\eta\text{-C}_5\text{H}_6(\textit{syn}\text{-Et-}5)\}]^+$ (**12**) containing an acyclic 5-ethylpentadienyl ligand, as shown by X-ray crystallography.

Highly electrophilic transition metal centres may satisfy their electronic requirements by forming an intramolecular, three-centre interaction (agostic) with the σ -electrons of an adjacent C–H bond.¹ The C–H bonds in such systems are often cleaved reversibly and rapidly on the n.m.r. time scale. Protonation of co-ordinated ethylene in cobalt(I) complexes of the type $[\text{Co}(\eta\text{-C}_5\text{Me}_4\text{R})(\eta\text{-C}_2\text{H}_4)\text{L}]$ ($\text{R} = \text{Me}, \text{Et}; \text{L} = \text{C}_2\text{H}_4; \text{R} = \text{Me}, \text{L} = \text{PR}_3$) gives cobalt(III) complexes containing agostic ethyl groups.^{2,3,4} In extending this work to more complex hydrocarbon ligands, we have discovered that a sequence of protonation, hydride addition, and re-protonation induces two successive C–C bond cleavages in co-ordinated norbornadiene (C_7H_8) (Scheme 1).[†] Although the C–C bonds of highly strained hydrocarbons are known to be cleaved by soluble transition metal complexes,⁵ few examples are known for unstrained systems.⁶ Our work shows that this process can occur both in norbornenyl and in a relatively unstrained C_5 ring.

[†] All new complexes were characterized by n.m.r. (^1H , ^2H , ^{13}C , and $^{13}\text{C}\{^1\text{H}\}$) spectroscopy and, for those complexes stable at room temperature, by elemental analyses. Selected n.m.r. spectroscopic data for key complexes are as follows [chemical shifts in p.p.m. (δ), coupling constants, $J(\text{HH})$ (^1H n.m.r.) and $J(\text{CH})$ (^{13}C n.m.r.) in Hz].

(**2**): ^1H n.m.r. (CD_2Cl_2 , -80°C) δ 2.70, 2.69 (overlapping m, 3H, H^2 , H^6 , H^1 or H^4), 4.34 (m, 2H, H^3 , H^5), 4.06 (m, 1H, H^1 or H^4), -9.38 (s, CoH).

(**3**): ^1H n.m.r. (CD_2Cl_2 , -45°C) δ 2.68 (m, 1H, H^1 or H^4), 2.72 (m, 2H, H^2 , H^6), 4.35 (m, 2H, H^3 , H^5), -9.33 (t, 1H, J 13, Co–H–C).

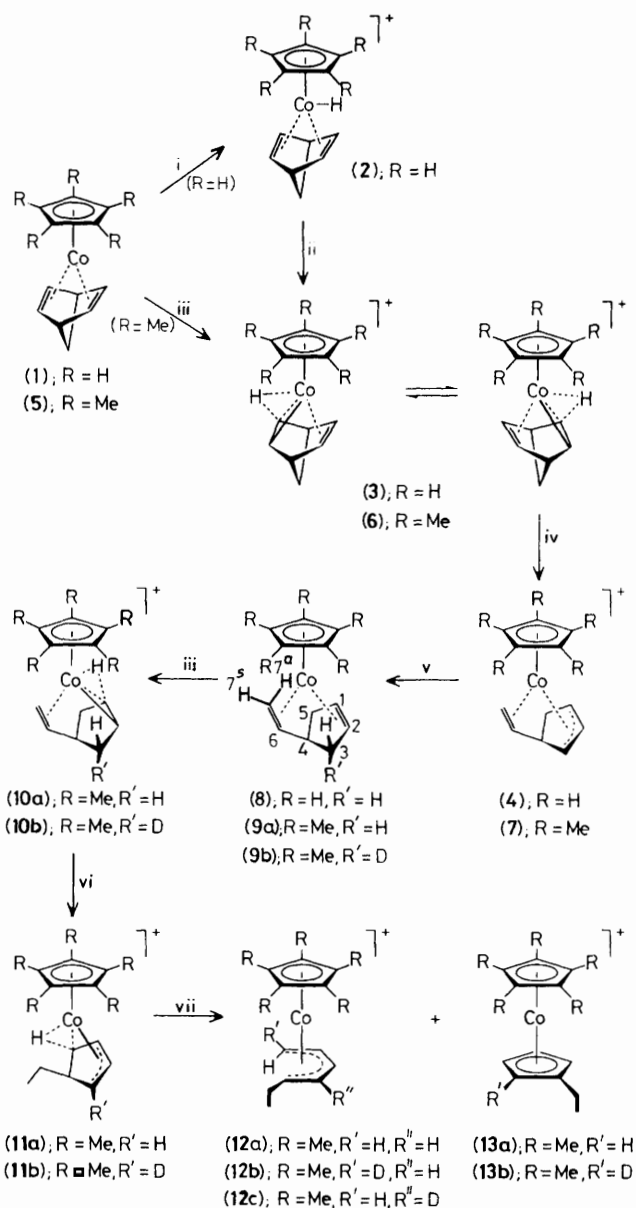
(**6**): ^1H n.m.r. (CD_2Cl_2 , -70°C) δ 2.39 (d, 2H, J 11.8, H^2 , H^6), -8.72 (t, 1H, J 12, Co–H–C); ^{13}C n.m.r. δ 43.0 (d, J 190, C^3 , C^5), 29.5 (dd, J 170, 46, C^2 , C^6).

(**9a**): ^1H n.m.r. (C_6D_6 , 25°C) δ 2.76 (dd, 1H, J 4.2, 1.4, H^2), 2.57 (d, 1H, J 11, H^{7a}), 2.40 (ddd, 1H, J 11.2, 7.5, 2.1, H^6), 2.29 (dd, 1H, J 11.1, 1.4, H^3 *endo*), 1.95 (d, 1H, J 11.1, H^3 *exo*), 1.70 (d, 1H, J 4.2, H^1), 1.50 (s, 16H, C_5Me_5 , H^4), 1.36 (d, 1H, J 7.5, H^{7b}), 1.03 (d, 1H, J 12.3, H^5 *endo*), 0.49 (d, 1H, J 12.2, H^5 *exo*); ^{13}C n.m.r. δ 91.8 (C_5Me_5), 76.3 (d, J 157, C^6), 65.0 (d, J 160, H^2), 49.9 (t, J 154, C^7), 49.3 (d, J 166, C^1), 44.8 (t, J 125, C^3), 35.2 (d, J 140, C^4), 30.0 (t, J 128, C^5), 9.7 (C_5Me_5).

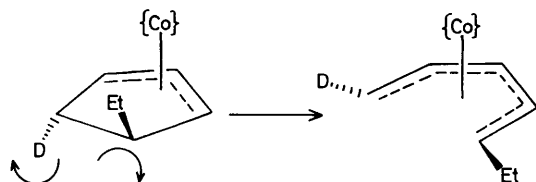
(**9b**): as (**9a**) except ^1H δ 2.29 (s), no resonance at δ 1.95; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. δ 44.8 [t, $J(\text{CD})$ 19]; ^2H n.m.r. (C_6H_6) δ \sim 2.3.

(**11a**): ^1H n.m.r. (CD_2Cl_2 , 25°C) δ 2.74 (d, 2H, J 10.1, H^2), 2.29 (dt, 1H, J 10.9, 6.8, H^3), -12.27 (dt, 1H, J 10.2, 10.8, Co–H–C); (-85°C) -12.46 (dd, 1H, J 20.5, 10.9, Co–H–C); ^{13}C n.m.r. (-85°C) δ 102.0 (d, J 176, C^2), 79.6 (d, J 182, C^1), 75.5 (d, J 174, C^3), 58.2 (d, J 136, C^4), 25.9 (t, J 126, C^6), 12.0 (q, J 127, C^7), 9.9 (dd, J 160, 90, C^5).

(**11b**): ^2H n.m.r. (CH_2Cl_2 , 25°C) (ref. C_6D_6 at δ 7.35) 1 peak at δ 2.7.



Scheme 1. Reagents and conditions: i, $\text{HBF}_4\cdot\text{OEt}_2$, HPF_6 , $\text{CF}_3\text{CO}_2\text{H}$, or $\text{CF}_3\text{SO}_3\text{H}$ at -80°C ; ii, -45°C ; iii, $\text{HBF}_4\cdot\text{OEt}_2$ at -68°C ; iv, -20°C ; v, LiAlH_4 (**8**), LiBHET_3 (**9a**), LiBDEt_3 (**9b**); vi, 0°C ; vii, 60°C , 8 h.



Scheme 2

Reaction of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(2,3:5,6\text{-}\eta\text{-C}_7\text{H}_8)]$ (**1**) with $\text{HBF}_4 \cdot \text{OEt}_2$, HPF_6 , $\text{CF}_3\text{CO}_2\text{H}$, or $\text{CF}_3\text{SO}_3\text{H}$ at -80°C gives a yellow solution which shows a single hydride resonance; at -45°C this changes to a triplet and the species present is the fluxional agostic cation $[\text{Co}(\eta\text{-C}_5\text{H}_5)(2:5,6\text{-}\eta\text{-C}_7\text{H}_9)]^+$ (**3**).⁷ The spectrum at -80°C is due either to the slowing of the "side-to-side" migration of the agostic hydride in (**3**) or to an intermediate terminal hydrido-cation (**2**). At -20°C , (**3**) undergoes rapid C-C bond cleavage to form quantitatively the 4-vinylcyclopentenylcobalt(III) cation $[\text{Co}(\eta\text{-C}_5\text{H}_5)(1\text{-}3:6,7\text{-}\eta\text{-CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2)]^+$ (**4**), which is stable at room temperature and can be isolated almost quantitatively as its BF_4 salt. The structure of $[(\mathbf{4})]\text{BF}_4$ has been determined by X-ray crystallography (Figure 1).[‡] Similar protonation of $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(2,3:5,6\text{-}\eta\text{-C}_7\text{H}_8)]$ (**5**) at -68°C gives the agostic cation $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(2:5,6\text{-}\eta\text{-C}_7\text{H}_9)]^+$ (**6**), which also rearranges at -20°C to give $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(1,3:6,7\text{-}\eta\text{-CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2)]^+$ (**7**).

N.m.r. spectra (^1H , ^{13}C) show that the solution formed from $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(2,3:5,6\text{-}\eta\text{-C}_7\text{H}_8)]$ and $\text{CF}_3\text{CO}_2\text{H}$ at room temperature contains the rhodium(III) analogue of (**4**), not the norborn-5-en-2-ylrhodium(III) cation suggested earlier.⁸ Thus the protonation behaviour of the neutral η -cyclopentadienyl(norbornadiene) complexes of cobalt(I) and rhodium(I) closely resembles that recently reported for the rhodacarborane(norbornadiene) anion $[\text{closo-}3,3\text{-}(2,3:5,6\text{-}\eta\text{-C}_7\text{H}_8)\text{-}1,2\text{-Me}_2\text{-}3,1,2\text{-RhC}_2\text{B}_9\text{H}_9]^-$,⁹ although mechanistically the reactions differ as in the latter case *exo*-proton attack was apparently observed.

[‡] Crystal data; $[(\mathbf{4})]\text{BF}_4$, $\text{C}_{12}\text{H}_{14}\text{BCoF}_4$, deep red crystals, $0.07 \times 0.09 \times 0.22$ mm, monoclinic, space group $P2_1/n$, $a = 12.105(2)$, $b = 9.928(2)$, $c = 10.346(2)$ Å, $\beta = 101.08(1)^\circ$, $U = 1220.2$ Å³, $Z = 4$, $D_c = 1.65$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 14.3$ cm⁻¹. Data were collected on a Philips PW 1100/20 diffractometer and corrected for absorption. Computer programs within the ANUCRYS structure determination package were used for structure solution and refinement. Final values of $R = 0.036$ and $R_w = 0.040$ were obtained for 1311 reflections with $I > 3\sigma(I)$ ($2\theta_{\text{max}} = 50^\circ$). Anisotropic temperature factors were used for non-hydrogen atoms during the full-matrix refinement. Some disorder of the fluorine atoms was observed. Hydrogen atoms of the C_7H_9 group were located in a difference electron-density map and cyclopentadienyl hydrogen atoms were located geometrically; hydrogen atom parameters were not refined.

For $[(\mathbf{12a})]\text{BPh}_4$, $\text{C}_{41}\text{H}_{46}\text{BCo}$, deep red crystals, $0.10 \times 0.12 \times 0.38$ mm, orthorhombic, space group $Pcab$, $a = 16.595(5)$, $b = 18.012(7)$, $c = 22.302(8)$ Å, $U = 6666(4)$ Å³, $Z = 8$, $D_c = 1.21$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 5.12$ cm⁻¹. Data were collected on a Nicolet R3m/V diffractometer. Structure solution and refinements were carried out using SHELXTL. The weakly diffracting nature of the crystal resulted in a relatively small number of data. Convergence to final values of $R = 0.073$ and $R_w = 0.070$ was obtained using 1075 reflections $I > 3.5\sigma(I)$. The structure was refined using full-matrix least squares, with all atoms isotropic except for Co. The phenyl groups were refined as rigid bodies and hydrogen atoms were included in calculated positions but not refined. There was some evidence of disorder in the ethyl group as shown by high thermal parameters. No correction was made for absorption. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

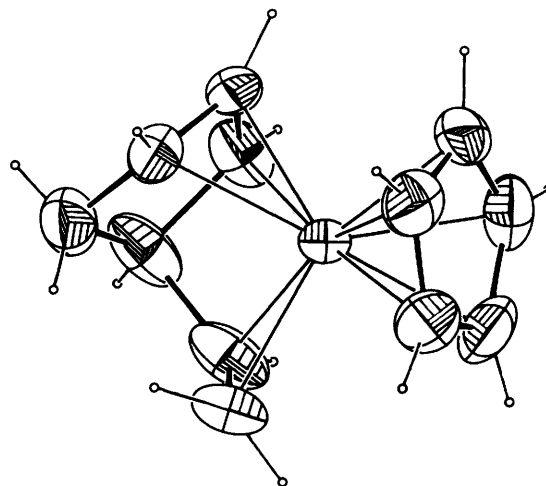


Figure 1. Molecular structure of cation (**4**) as its BF_4 salt. Selected bond lengths (Å) and angles ($^\circ$): Co-C(1) 2.137(5), Co-C(2) 2.132(5), Co-C(4) 2.146(5), Co-C(5) 2.009(4), Co-C(6) 2.145(5), Co-C₅ (mean) 2.063(5), C(1)-C(2) 1.341(7), C(2)-C(3) 1.549(8), C(3)-C(4) 1.520(7), C(4)-C(5) 1.372(7), C(5)-C(6) 1.401(7), C(6)-C(7) 1.507(8), C(7)-C(3) 1.507(8); C(1)-C(2)-C(3) 123.1(6), C(2)-C(3)-C(4) 95.5(5), C(2)-C(3)-C(7) 108.2(4), C(4)-C(3)-C(7) 103.1(5), C(3)-C(4)-C(5) 109.8(5), C(4)-C(5)-C(6) 108.1(5), C5-C(6)-C(7) 107.3(5), C(6)-C(7)-C(3) 101.9(5).

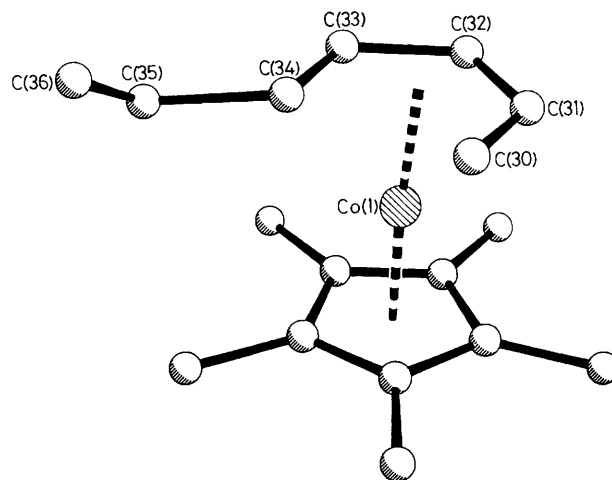


Figure 2. Molecular structure of cation (**12a**) as its BPh_4 salt. Selected bond lengths (Å) and angles ($^\circ$): Co-C(30) 2.07(2), Co-C(31) 2.00(2), Co-C(32) 2.03(2), Co-C(33) 2.03(3), Co-C(34) 2.16(3), Co-C₅ (mean) 2.05(2); C(30)-C(31)-C(32) 121(2), C(31)-C(32)-C(33) 113(2), C(32)-C(33)-C(34) 121(3), C(33)-C(34)-C(35) 103(3).

Complexes (**4**) and (**7**) react with LiAlH_4 or LiBHET_3 at one of the terminal allylic positions [C(3)] to give the corresponding 4-vinylcyclopentene complexes (**8**) and (**9a**) respectively; the position of hydride attack was identified by reaction of (**7**) with LiBDEt_3 to give (**9b**). Other nucleophiles (MeLi , KCN , NaOMe) attack at the same position.

Low temperature protonation of (**9a**) occurs at the internal double bond to give $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(2:6,7\text{-}\eta\text{-CH}_2=\text{CHCHCH}_2\text{CHCH}_2\text{CH}_2)]^+$ (**10a**), which contains an agostic bond to the *endo*-hydrogen atom on C(1). Complex (**10a**) undergoes a rapid double hydride shift as the temperature is raised to 0°C forming the 4-ethylcyclopentenyl complex

(11a) in which the agostic hydrogen atom exchanges rapidly between C(3) and C(5) above -80°C .

On heating to 60°C for 8 h (11a) undergoes carbon-carbon bond cleavage to form acyclic $[\text{Co}(\eta\text{-C}_5\text{Me}_5)\{\eta\text{-C}_5\text{H}_6(\text{syn-Et-5})\}]^+$ (12a). This is accompanied by $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\eta\text{-C}_5\text{H}_4\text{Et})]^+$ (13a), which is formed by loss of dihydrogen from (11a); the ratio of (12a) to (13a) is 2:1. A single crystal *X*-ray diffraction study \ddagger of [(12a)]BPh₄, formed by metathesis of [(12a)]BF₄ with NaBPh₄, establishes unequivocally the acyclic nature of the C₇ ligand and the *syn* orientation of the ethyl group (Figure 2). Similarly, reaction of (9b) with HBF₄ and heating of the intermediates (10b) and (11b) affords the three products (12b), (12c), and (13b) with deuterium in the positions shown in Scheme 2. In (12b) it is evident that ring opening has occurred with conrotatory motion (Scheme 2), which is contrary to the Woodward-Hoffmann rules for the cyclopentenyl anion but consistent with them for the corresponding cation.^{10,11}

We^{3a} have already noted that a solution of the agostic cobalt-alkyl complex $[\text{Co}(\eta\text{-C}_5\text{Me}_5)\text{Et}\{\text{P}(p\text{-tolyl})_3\}]^+$ catalyses ethene polymerization. Schmidt and Brookhart⁴ have demonstrated the sequential insertion of ethene in similar agostic cobalt-alkyl complexes and have provided an explanation for the relationship between an agostic M-H-C ground state and a low activation barrier to C-C bond formation. A corollary of this is that the activation barrier to the reverse reaction, namely C-C bond cleavage, should also be lowered; the formation of (12) demonstrates that this can occur easily even in a relatively unstrained ring in an agostic complex. It is reasonable to postulate that the transition state for this reaction contains a 3-centre, 2-electron Co-C-C interaction involving the electrons of the C(3)-C(4) [or C(4)-C(5)] bond in complex (11), analogous to the Co-H-C bond which represents the ground state in complexes (3), (6), (10) and (11).

We thank the S.E.R.C. for a studentship (J. C. N.) and support.

Received, 6th April 1989; Com. 9/01423C

References

- 1 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395; M. Brookhart, M. L. H. Green, and L-L. Wong, *Progr. Inorg. Chem.*, 1988, **36**, 1.
- 2 M. Brookhart, M. L. H. Green, and R. B. A. Parry, *J. Chem. Soc., Chem. Commun.*, 1983, 691.
- 3 (a) R. B. Cracknell, A. G. Orpen, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1984, 326; (b) R. B. Cracknell, A. G. Orpen, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1986, 1005.
- 4 G. F. Schmidt and M. Brookhart, *J. Am. Chem. Soc.*, 1985, **107**, 1443.
- 5 K. C. Bishop, *Chem. Rev.*, 1976, **76**, 461.
- 6 R. H. Crabtree, R. P. Dion, D. J. Gibboni, D. V. McGrath, and E. M. Holt, *J. Am. Chem. Soc.*, 1986, **108**, 7222; J. E. Bercaw, E. Bunel, and B. J. Burger, *J. Am. Chem. Soc.*, 1988, **110**, 976, and references cited therein.
- 7 Rapid 'side to side' migration has also been postulated to occur in the corresponding norbornenyl-iron complex $[\text{Fe}(\text{CO})_3(2:5,6\text{-}\eta\text{-C}_7\text{H}_9)]^+$: M. Brookhart and D. L. Harris, *Inorg. Chem.*, 1974, **13**, 1540; G. A. Olah, S. H. Yu, and G. Liang, *J. Org. Chem.*, 1976, **41**, 2383.
- 8 J. Evans, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 510.
- 9 D. M. Speckman, C. B. Knobler, and M. F. Hawthorne, *Organometallics*, 1985, **4**, 1692.
- 10 R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie-Academic Press, Weinheim, 1970.
- 11 Examples of soluble transition metal complexes that mediate strained C-C bond cleavage by formally forbidden rotation have been reported: A. R. Pinhas, A. G. Samuelson, R. Risemberg, E. V. Arnold, J. Clardy, and B. K. Carpenter, *J. Am. Chem. Soc.*, 1981, **103**, 1668.