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Communications

The First Crystal Structure of a Nickel Cyclopropene Complex[†]

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Summary: Nickel(0) cyclopropene complexes are usually only detected as reactive intermediates during the oxidative cyclization of cyclopropenes at the Ni(0) site. In contrast, it was possible to isolate and structurally characterize such a Ni(0) cyclopropene complex from the reaction of [(bipy)Ni(COD)] with dimethyl 3-methyl-3-tert-butyl-1-cyclopropene-1,2-dicarboxylate.

In our ongoing work in investigating the mechanism of the reactions of nickel(0) complexes with unsaturated substrates,[1,2] we have more recently become interested in studying the oxidative coupling of cyclopropene derivatives at the nickel(0) site. It is well-known, from the studies of Binger and co-workers, that $[((C_6H_5)_3P)_2$-Ni(COD)] catalyzes the $[2\pi + 2\pi]$ cycloaddition of strained-ring alkenes to give cyclobutane derivatives: e.g. 3,3-dimethylcyclopropene (**1**; $R^1 = CH_3$, $R^2 = H$) reacts to give 3,3,6,6-tetramethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexane (**6**; $R^1 = CH_3$, $R^2 = H$).[3−8] The proposed mechanism for this reaction is shown in Figure 1 ($L_n = ((C_6H_5)_3P)_n$).[8]

The synthesis of the intermediate **2** (with $(C_6H_5)_3P$ as coligands L) together with ^{1}H NMR data for the two complexes with $R^1 = R^2 = CH_3$ and $R^2 = H$ and CH_3 and $R^1 = CH_3$ in the cyclopropene ligand was described earlier, but no crystal structure was reported.[9]

Using [(bipy)Ni(COD)] (L_n = bipy = bipyridine in Figure 1), it was possible to isolate α,α′-bipyridyl-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane (**4**; Figure 1, $R^1 = CH_3$, $R^2 = H$). **4** was characterized by ^{1}H NMR spectroscopy and X-ray crystallography.[7]

In our kinetic studies we have started to investigate the mechanism of the reaction of [(bipy)Ni(COD)] with

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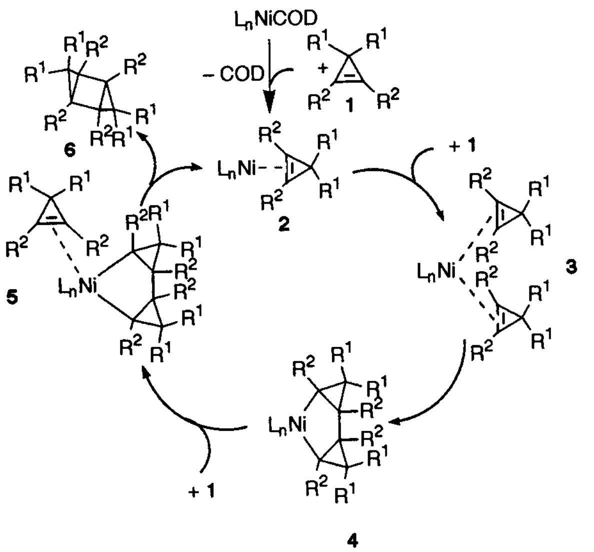

Figure 1. Proposed mechanism for the catalytic oxidative cyclization of cyclopropenes with Ni(0) complexes.

dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate (**1**; $R^1 = CH_3$, $R^2 = COOCH_3$), using stopped-flow techniques.[10] During these measurements we found kinetic evidence for the formation of **2** followed by oxidative cyclization to the corresponding 5-nickela-*trans*-tricyclo-[4.1.0.0^{2,4}]heptane complex (**4**; $R^1 = CH_3$, $R^2 = COOCH_3$).

To confirm the findings above, we prepared the sterically more demanding dimethyl 3-methyl-3-*tert*-butyl-1-cyclopropene-1,2-dicarboxylate (**1**; $R^1 = CH_3$, $C(CH_3)_3$, $R^2 = COOCH_3$), which was found not to undergo oxidative cyclization with palladium(0), and reacted it with [(bipy)Ni(COD)] at room temperature.[11] This approach allowed us to isolate the intermediate **2** as a solid and to structurally characterize it.[11] An ORTEP plot of **2** ($R^1 = CH_3$, $C(CH_3)_3$, $R^2 = COOCH_3$) is shown in Figure 2.

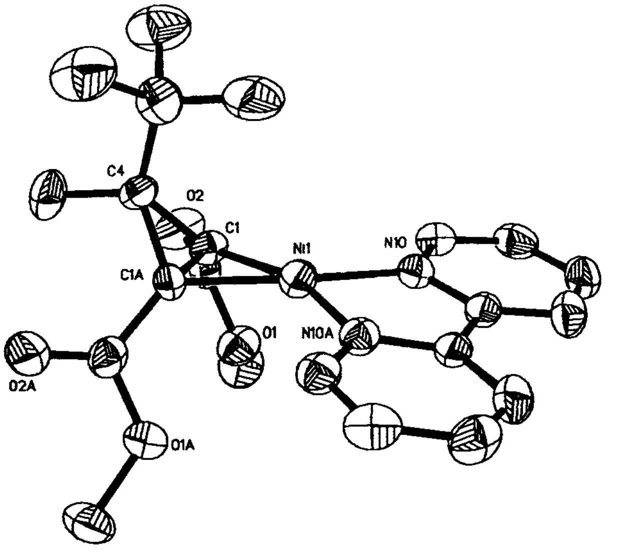

Figure 2. ORTEP plot of **2** (thermal ellipsoids at 50% probability). Selected bond angles (in deg; selected bond lengths are given in the text): C(1)–Ni(1)–C(1)#, 44.5(3); N(10)#1–Ni(1)–N(10), 82.9(2); angle between planes of C(1)–Ni(1)–C(1)# and C(1)–C(4)–C(1)#, 126.4°.

The structure of **2** shows characteristic trigonal-planar Ni(0) geometry with Ni–C_{olefin} distances of 1.897(5) Å, Ni–N distances of 1.911(4) Å, and a C–C (olefin) distance of 1.437(9) Å (there is a plane of symmetry in the molecule). The bond lengths are at the lower end of the range typically found for the large number of structurally characterized Ni(0) olefin complexes (only some selected examples are given in ref 13–19). Ittel's and Iber's structural parameters α and β characterize the hybridization changes at the coordinated olefinic bonds and were found to be $\alpha = 87.3°$ and $\beta = 46.3°$.[20] Clearly, the two methoxycarbonyl groups are bent out of the plane of the complexed cyclopropene ring. It is noteworthy to point out that the *tert*-butyl group in **2** is *endo*, which arises most likely from the fact that an attack of the metal ion from the other, more readily accessible side would lead to a *cis* arrangement of the ester and the *tert*-butyl group (thermodynamic control). So far, very few cyclopropene complexes have been structurally characterized. In such complexes the metal center is platinum(0) with Pt–C_{olefin} distances varying from 1.98(5) to 2.21(5) Å and C–C (olefin) distances ranging between 1.434(12) and 1.50(1) Å, similar to those found in **2**.[21–23]

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(11) Dimethyl 3-methyl-3-*tert*-butyl-1-cyclopropene-1,2-dicarboxylate (**1**; $R^1 = CH_3$, $C(CH_3)_3$, $R^2 = COOCH_3$): 750 mg (4.03 mmol) of 2-methoxy-2,5-dimethyl-5-*tert*-butyl-(Δ^3)-1,3,4-oxadiazoline[12] and 710 mg (5.00 mmol) of dimethyl acetylenedicarboxylate in 100 mL of diethyl ether were irradiated with a Heraeus TQ150 mercury lamp in a normal glass apparatus for 6 h. Then the solvent was removed under vacuum, and the crude product was separated by column chromatography on silica gel: 184 mg (25%) of the starting material (oxadiazoline) and 370 mg (54%) of **1** were isolated as colorless oils. R_f(hexane/ethyl acetate, 3:1) = 0.51. IR (film, NaCl): 2963, 2871, 1828, 1715, 1436, 1248, 1118, 1079, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.94 (s, 9 H), 1.35 (s, 3 H), 3.86 (s, 6 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 19.8 (q), 28.4 (q, 3 C), 35.4 (s), 43.3 (s), 52.5 (q, 2 C), 130.3 (s, 2 C), 160.5 (s, 2 C). Anal. Calcd for $C_{12}H_{18}O_4$ (226.3): C, 63.70; H, 8.02. Found: C, 63.79; H, 8.06. **2** ($R^1 = CH_3$, $C(CH_3)_3$, $R^2 = COOCH_3$): in a glovebox 136 mg of **1** ($R^1 = CH_3$, $C(CH_3)_3$, $R^2 = COOCH_3$) (0.6 mmol) in 5 mL of THF were added to a solution of 135 mg of [(bipy)Ni(COD)] (0.42 mmol) in 10 mL of THF with stirring. Crystals suitable for X-ray characterization were obtained by diffusion of ether into that solution (yield 129 mg (70%)). ^1H NMR (THF-d_8, 300 MHz): δ 0.94 (s, 9 H), 1.85 (s, 3 H), 3.80 (s, 6 H), 7.42 (br m, 2 H), 8.02 (br m, 2 H), 8.12 (br m, 2 H), 8.91 (br m, 2 H). Due to decomposition of the sensitive compound after some time, additional NMR signals start to build up and line broadening is observed. Anal. Calcd for $C_{22}H_{26}N_2NiO_4$·THF (the sample contained THF from washing the crystals): C, 60.84; H, 6.68; N, 5.46. Found: C, 60.82; H, 6.71; N, 5.42. Crystal structure analysis of **2**: $C_{22}H_{26}N_2NiO_4$, $M_r = 441.16$, orthorhombic, space group *Pnma*, $a = 7.5385(7)$ Å, $b = 15.3049(15)$ Å, $c = 17.806(2)$ Å, $V = 2054.4(4)$ Å^3, $\alpha = \beta = \gamma = 90°$, $\rho_{calcd} = 1.420$ g cm^{-3}, $Z = 4$, crystal size $0.15 \times 0.10 \times 0.02$ mm, Nonius KappaCCD area detector, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $T = 173(2)$ K, graphite monochromator, scan range $4.6° < 2\theta < 50.0°$. Absorption effects were corrected with SCALEPACK.[24] Of 3325 collected reflections, 1885 were independent and 911 had $I > 2\sigma(I)$. The structure was solved by direct methods, and all non-hydrogen atoms were refined by full matrix least-squares methods on F^2 (SHELXL 97).[25] The hydrogen atoms were fixed in idealized positions using a riding model. There were 141 refined parameters in all, with $R1 = 0.0536$ ($F_o > 4\sigma(F_o)$) and $wR2 = 0.1286$ (all data).

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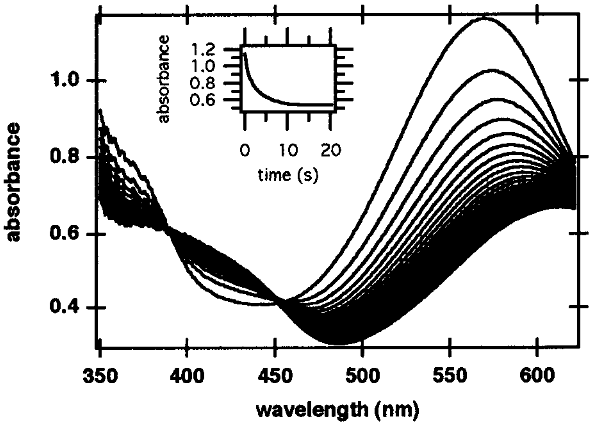

Figure 3. Time-resolved spectra of the reaction of *tert*-butylmethylcyclopropene-1,2-dicarboxylate with [(bipy)Ni(COD)] ([complex] = 0.25 mM, [cyclopropene] = 20 mM, $\Delta t = 0.4$ s, $T = 20.0$ °C). The insert shows the absorbance vs time trace at 560 nm.

The formation of **2** can be followed by UV−vis spectroscopy using stopped-flow techniques. Time-resolved spectra for the reaction of [(bipy)Ni(COD)] with **1** ($R^1 = CH_3, C(CH_3)_3, R^2 = COOCH_3$) at 20.0 °C are shown in Figure 3.

The reaction follows the simple rate law d[(bipy)Ni(COD)]/dt = k[(bipy)Ni(COD)][cyclopropene], with $k = 17.0 \pm 0.8$ M^{-1} s^{-1}. The reaction is only slightly slower (2-fold) compared to the reaction of [(bipy)Ni(COD)] with the less substituted **1** ($R^1 = CH_3$, $R^2 = COOCH_3$). A detailed kinetic analysis of these reactions will be reported elsewhere.[10]

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Supporting Information Available: Tables giving crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (without structural factors) for **2** have been deposited as Supplementary Publication No. CCDC-150787 at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21 EZ, U.K. (fax, int. code + 1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

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