Cyclopropane and its derivatives (ER₂₃) (E = C, Si, Ge, Sn), bicyclooctanes, and other strained hydrocarbons have remarkably low oxidation potentials when compared to their unstrained linear counterparts.¹–³ Can this property be translated to transition-metal complexes, such that small rings incorporating the transition metal lead to more facile oxidation? With this question in mind, we characterized a d⁸Rh complex that has a metal center incorporated in a three-membered ring. Furthermore, we report the results from high-resolution pulse EPR spectroscopy, which, in combination with density functional theory (DFT) calculations, allowed us to characterize in detail the electronic structure of the corresponding radical cation.

In analogy to the preparation of tropNH²⁴ (trop = tropylidenyl = 5H-dibenz[a,d]cyclohepten-5-yl), we prepared the N-methyl derivative tropNMe (1) from (Me₃Si)₂NMe and tropCl (Scheme 1). Subsequently, 1 was treated with [Rh₂(µ-Cl)₂(cod)] (cod = 1.5-cyclooctadiene) to yield [Rh₂(µ-Cl)₂(trop,NMe)₂], which was treated with PPh₃ to give [RhCl(trop,NMe)(PPh₃)] (2). Addition of AgOTf (OTf⁻ = CF₃SO₃⁻) led to the isolation of [Rh(trop,NMe)(PPh₃)]OTf (3) as red needles in 78% overall yield (for details, see the Supporting Information). The [¹³C] and [D₃] labeled iodide complexes [¹³C]5 and [D₃]5 were prepared from the reactions of the rhodium(i)amide 4⁵ with [¹³CH₃]I and CD₃I, respectively. The NMR data indicate that 2 and 5 form trigonal bipyramidal 18-electron complexes in CDCl₃ solution with the halide atoms and the C=Cₜ₉ units in the equatorial positions. Complex 3 forms an ion pair in solution, such that the OTf⁻ ion binds remotely from the metal in a pocket between the NMe group and the benzylic protons of the trop,NMe ligand.

An ion pair is also observed for 3 in the solid state, again with the OTf⁻ ion bound remotely from the metal center and embedded between the arene groups of the tropylidenyl and PPh₃ ligands (Figure 1b).⁶ The [Rh(trop,NMe)(PPh₃)]⁺ ion has an unusual “saw-horse” structure (Figure 1a) which is nonplanar and resembles a trigonal bipyramidal with one equatorial ligand missing (selected bond lengths and angles are listed in Table 1). Structures of this type have rarely been observed for stable 16-electron complexes; some examples include the neutral amide 4⁷ and the Ru complexes [Ru(CO)₂L₂] (I) and [Ru(CO)(NO) L₂]⁻ (II; L = PrBu₃Me)⁷. The N-Rh-P bond angle in 3 (158.2(1)°) and the P-Ru-P bond angle in II (157.3(8)°) are slightly more acute than the corresponding bond angles in the neutral complexes 4 (166.2°) and I (165.6°). The ct-Rh-ct angle (134.5(2)°, ct = centroid of the coordinated double bond) is similar to the corresponding angles in 4 and I (ca. 135°), but larger than that.

in the nitrosyl complex II (120°). The small Rh1-P1-C200 angle (86.1(2)°) and relatively short Rh···C200 distance (2.80 vs. >3.6 DCIHO for the other Rh···Cphenyl distances) in 3 are especially noteworthy and indicate a hyperconjugative interaction between the P/C0 C bond and the metal center.

The triflate complex 3 reacts cleanly with KOTBu to give complex 6. The compounds [13C]6 and [D2]6, in which the N-methylene group is 13C- and D-labeled, were obtained from the respective iodide complexes [13C]5 and [D3]5. The result of an X-ray structure analysis on orange crystals of 6 is shown in Figure 2; selected bond lengths and angles are given in Table 1.

Interactions between a metal M and an unsaturated ligand X=Y can be considered with regard to the limiting cases represented by the heterocyclic metallacyclopropane form (type A, Scheme 2) and a X=Y>M donor–acceptor complex (type B).

Complex 6 can be described either as a rhodazaacyclop propane 6A or a rhodium iminium ion complex 6B. In the first case, the Rh center has a formal oxidation state of +1, and in the latter case a formal oxidation state of −1.

The Rh–N bond in 6 (2.059(3) Å) is shorter than in 3 (2.131(5) Å). Also, the N–CH3 bond in 6 (1.446(5) Å) is significantly shorter than the N–CH3 bond in 3 (1.505(7) Å), but considerably longer than the N–C bonds in iminium ions (1.274–1.301 Å) and close in length to the N–C bonds in aziridines (1.440–1.471 Å). Hence, the structural data favor the rhodazaacyclop propane description 6A, which is expected in view of the energetically low-lying π* orbital of the N–C bond and the consequently strong metal-to-ligand back donation.

Table 1: Selected bond lengths [Å] and angles [°] of 3 (experimental), 6 (experimental), and 6+ (calculated by DFT).

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<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3exp</td>
<td>–</td>
<td>2.131(5)</td>
<td>1.505(7)</td>
<td>2.254(1)</td>
<td>2.075(4)</td>
<td>1.413(6)</td>
<td>158.2(1)</td>
<td>134.5(2)</td>
<td>103.1(3)</td>
<td>–</td>
</tr>
<tr>
<td>6exp</td>
<td>2.117(4)</td>
<td>2.059(3)</td>
<td>1.446(5)</td>
<td>2.254(1)</td>
<td>2.065(3)</td>
<td>1.419(4)</td>
<td>160.35(9)</td>
<td>132.6(1)</td>
<td>71.9(2)</td>
<td>67.6(2)</td>
</tr>
<tr>
<td>6+calc</td>
<td>2.090</td>
<td>2.164</td>
<td>1.417</td>
<td>2.267</td>
<td>2.179</td>
<td>1.422</td>
<td>158.50</td>
<td>136.05</td>
<td>67.75</td>
<td>38.88</td>
</tr>
</tbody>
</table>

[a] ct indicates the midpoint of the coordinated C=Ctrop bond.
A cyclic voltammogram recorded in a THF solution (0.1 M nBu4NPF6 electrolyte, T = 298 K, Pt electrode, scan rate 100 mV s⁻¹) of the rhodaazacyclopropane 6 showed one reversible wave at a remarkably low potential (E₁/₂ = −0.510 V vs. the ferrocenium/ferrocene couple), corresponding to the oxidation 6 → 6⁺.[12] The high stability of 6⁺ allowed the first detailed study of the electronic structure of a rhodaazacyclopropyl radical cation by continuous-wave (CW) and pulse EPR spectroscopy.[13] For this study, 6 as well as the ¹³C- and D₂-labeled derivatives [¹³C]6 and [D₂]6 were oxidized with ferrocenium triflate to give the radical cations 6⁺, [¹³C]6⁺, and [D₂]6⁺, respectively. The half-life of 6⁺ in THF solution (ca. 0.1 M) is about five hours at room temperature.[14]

The frozen-solution X-band CW-EPR spectra of 6⁺ and [¹³C]6⁺ are shown in Figure 3a. Both spectra are well-resolved at the high-field end (g₂ = 2.0155, g₁ = 2.0145) and show splittings from the ¹⁰³Rh nucleus (I = 1/2) for 6⁺ and from the ¹⁰³Rh and ¹³C nuclei (I = 1/2) for [¹³C]6⁺. At the low-field end (g₁ = 2.121), the spectra are poorly resolved.[15] Pulse ENDOR (electron nuclear double resonance) and HYSCORE (hyperfine sublevel correlation) spectroscopies were used to determine the complete set of hyperfine parameters of the ¹⁰³Rh and ¹³C nuclei of the methylene unit, as well as of the two methylene ¹H nuclei, the weakly coupled ¹⁴N nucleus, the olefinic ¹³C nuclei, the olefinic protons, and the ³¹P nucleus (see the Supporting Information). To assign the methylene proton signals unambiguously, the corresponding spectra of [D₂]6⁺ were also recorded (Supporting Information).

In Figure 3b, a representative hyperfine-correlated ENDOR (HYEND) spectrum of [¹³C]6⁺ is displayed which contains ¹⁰³Rh and ¹³C ENDOR frequencies (νENDOR axis) that are correlated with their corresponding hyperfine frequencies (νIF axis). In Figure 3c, a representative Q-band HYSCORE spectrum of 6⁺ is shown which contains peaks from the ¹⁰³Rh nucleus, the ¹³C nuclei of the olefinic C5 atoms, and the ¹⁴N and ³¹P nuclei. The EPR parameters were obtained from the spectrum by matching the position of the experimental cross-peaks with those calculated from the relevant spin Hamiltonian. A complete set of experimentally derived parameters is given in Table 2, along with the data obtained from DFT calculations.[16] The experimental spin populations were calculated from their respective hyperfine couplings.[17]

Overall, the agreement between experimentally derived and calculated EPR parameters and spin populations is excellent. According to the DFT calculations, the main part of the spin density is located on the rhodium center (47 %), the methylene carbon atom (14 %), and the four olefinic carbon atoms (C5 2 × 15 %, C4 2 × 3 %). This distribution of spin density can be seen by inspection of the spin-density plot.

Figure 3. a) Experimental (Exp.) and simulated (Sim.) second-derivative X-band CW-EPR spectra of 6⁺ and [¹³C]6⁺ in THF measured at 115 K. b) X-band HYEND spectrum of [¹³C]6⁺ in THF measured at 15 K at the observer position g₁. The dashed lines are separated by twice the nuclear Zeeman interaction (2ν) of ¹⁰³Rh and ¹³C, and cross the νENDOR and νIF axes at ν₁(¹⁰³Rh) and ν₁(¹³C), respectively. c) Q-band HYSCORE spectrum of 6⁺ in THF measured at 15 K near to the g₁ observer position. Cross-peaks from ¹³C (in natural abundance), ¹⁰³Rh, ³¹P, and ¹⁴N are labeled. d) Spin density of compound 6⁺, plotted with an isosurface level of 0.004.
Communications

Table 2: EPR parameters and spin populations of compound 6\textsuperscript{+}. DFT values are given in brackets.\textsuperscript{[11]}

<table>
<thead>
<tr>
<th>Group</th>
<th>Nucleus</th>
<th>A\textsubscript{x} [MHz]</th>
<th>A\textsubscript{y} [MHz]</th>
<th>A\textsubscript{z} [MHz]</th>
<th>Spin population</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>RhC</td>
<td>21 ± 2</td>
<td>25 ± 2</td>
<td>–18 ± 2</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(26.3)</td>
<td>(22.6)</td>
<td>(–12.2)</td>
<td>(47%)</td>
</tr>
<tr>
<td>methylene</td>
<td>C16</td>
<td>19 ± 2</td>
<td>20 ± 2</td>
<td>66 ± 2</td>
<td>15%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(16.3)</td>
<td>(47.8)</td>
<td>(14%)</td>
<td></td>
</tr>
<tr>
<td>amine</td>
<td>N1</td>
<td>–1.6 ± 0.2</td>
<td>0 ± 2</td>
<td>3 ± 1</td>
<td>2 ± 0.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(–7.9)</td>
<td>(0.1)</td>
<td>(2.4)</td>
<td>(2±0.1%)</td>
</tr>
<tr>
<td>PPh\textsubscript{3}</td>
<td>P1</td>
<td>0 to 15</td>
<td>0 to 15</td>
<td>0 to 15</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.4)</td>
<td>(4.3)</td>
<td>(17)</td>
<td>(2.5%)</td>
</tr>
<tr>
<td>olefin</td>
<td>C5</td>
<td>21 ± 5</td>
<td>21 ± 5</td>
<td>55 ± 5</td>
<td>2 ± 11%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(–0.2)</td>
<td>(–0.1)</td>
<td>(40.3)</td>
<td>(2±15%)</td>
</tr>
<tr>
<td>olefin</td>
<td>H5</td>
<td>–11 ± 1</td>
<td>4 ± 2</td>
<td>4 ± 1</td>
<td>2 ± 0.1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(–10.8)</td>
<td>(1.3)</td>
<td>(2.3)</td>
<td>(2±0.2%)</td>
</tr>
<tr>
<td>H4</td>
<td>5 ± 1</td>
<td>5 ± 2</td>
<td>10 ± 1</td>
<td>2 ± 0.5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3.5)</td>
<td>(5.2)</td>
<td>(9.3)</td>
<td>(2±0.3%)</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} The signs of the experimental hyperfine couplings A\textsubscript{ij}, are assigned according to the DFT results; principal axis directions are given in the Supporting Information. \( g_1 = 2.12100 \) (2.1050), \( g_2 = 2.01555 \pm 0.0005 \) (2.0174), \( g_3 = 2.0145 \pm 0.0005 \) (2.0163).

given in Figure 3d. There is some spin delocalization to the two benzo moieties (2 x 6.6%) of the trop ligand, with the alternating sign of the hyperfine couplings of adjacent carbon nuclei indicating a spin-polarization (hyperconjugation) mechanism. Both experimental and calculated data show small hyperfine couplings and thus small spin populations on the nitrogen and phosphorus nuclei. A comparison of 6 and 6\textsuperscript{+} shows that the gross structural features are retained.

In summary, X-ray, NMR, and EPR spectroscopic data strongly support the proposal that 6 and 6\textsuperscript{+} are best formulated as RhNC metallacycles. In such a formulation, the interaction of the filled \( \pi(C\text{--}N) \) orbital (polarized towards the N atom) with unoccupied metal orbitals represents the Rh–N bond, and the interaction of the unoccupied \( \pi^*(C\text{--}N) \) orbital (polarized towards the C atom) with occupied metal orbitals represents the Rh–C bond, which lies higher in energy. Therefore, oxidation of 6 mainly affects the Rh–C bond, and consequently the spin population at the carbon atom in 6\textsuperscript{+} is significant, but very low at the nitrogen atom.

It has been convincingly demonstrated that constraints imposed by the ligand sphere can be used to control the redox potential of transition-metal complexes\textsuperscript{[20]} and we have reported that four-coordinate d\textsuperscript{8} Rh complexes have large negative reduction potentials when the ligand sphere is not flexible enough to allow for a tetrahedral distortion.\textsuperscript{[20]}

However, as a result of a lack of suitable reference compounds, the present study does not allow the firm conclusion that small-ring metalla-heterocycles are more easily oxidized than corresponding larger-ring complexes or comparable acyclic precursors, and it remains an open question whether compounds such as 6 are strained molecules. Certainly, the coordination of the C=C\textsubscript{trop} units to the metal center also contributes to the low oxidation potential of 6 and the high stability of its radical cation 6\textsuperscript{+}.\textsuperscript{[20]}

An assignment of an oxidation state to the metal center in 6\textsuperscript{+} is not meaningful\textsuperscript{[21]} and this complex is best described as a radical with a delocalized unpaired electron.

Experimental Section

Selected spectroscopic data of diagnostic value are given; for details, see the Supporting Information.

3: CH\textsubscript{3}Cl (10 mL) and THF (10 mL) were added to [RhCl\textsubscript{3}(trop,NMe\textsubscript{2}PPh\textsubscript{3})] (162 mg, 0.200 mmol) and AgSO\textsubscript{4}CF\textsubscript{3} (51 mg, 0.200 mmol). The resulting red suspension was stirred at room temperature for 1 h and filtered over celite to remove AgCl. The solvents were evaporated in vacuo, and the residue was recrystallized from CH\textsubscript{3}Cl\textsubsuperscript{2}/hexanes to yield 6 (175 mg, 0.189 mmol, 94%) as red needles. M.p. >190°C (decomp); \textsuperscript{1}H NMR (300.1 MHz, CD\textsubscript{3}Cl\textsubscript{2}); \( \delta = 1.85 \) (d, \( J_{\text{HH}} = 2.9 \) Hz, 3H, CH\textsubscript{3}NCH\textsubscript{3}), 4.86 (dd, \( J_{\text{HH}} = 8.9 \) Hz, \( J_{\text{HH}} = 2.0 \) Hz, 2H, CH\textsubscript{2}), 6.61 ppm (dd, \( J_{\text{HH}} = 8.9 \) Hz, \( J_{\text{HH}} = 2.9 \) Hz, \( J_{\text{HH}} = 2.9 \) Hz, 2H, CH\textsubscript{2}), 11.1 ppm (s, NCH\textsubscript{3}), 78.6 ppm (d, 13C CH\textsubscript{2}), 88.5 ppm (d, 13C CH\textsubscript{2}) = 13.1 Hz, CH\textsubscript{2}), 110 ppm (121.5 MHz, CD\textsubscript{3}Cl\textsubscript{2}), \( \Pi = 39.2 \) ppm (d, \( J_{\text{HH}} = 138 \) Hz); Rh NMR (12.6 MHz, CD\textsubscript{3}Cl\textsubscript{2}); \( \Pi = 1272 \) ppm (d, \( J_{\text{HH}} = 138 \) Hz); HRMS (MALDI); m/z: 776.1975 (calcd for C\textsubscript{61}H\textsubscript{49}N\textsubscript{2}P\textsubscript{3}Rh\textsubscript{5}Cl\textsubscript{2}); 776.1948 (calcld for C\textsubscript{61}H\textsubscript{49}N\textsubscript{2}P\textsubscript{3}Rh\textsubscript{5}Cl\textsubscript{2}).

6: A solution of KO\textsubscript{Bu} (18.2 mg, 0.162 mmol) in THF (2 mL) was added to a suspension of 3 (150 mg, 0.162 mmol) in THF (5 mL). The resulting orange solution was filtered over a plug of alumina and concentrated to 1 mL under reduced pressure. The product crystallized upon addition of toluene (1 mL) and hexanes (10 mL). The mother liquor was decanted, and orange crystals of 6 were dried in vacuo. Yield: 88 mg (0.114 mmol, 70%); m.p. > 165°C (decomp); \textsuperscript{1}H NMR (300.1 MHz, CD\textsubscript{3}Cl\textsubscript{2}); \( \delta = 8.7 \) Hz, 2H, CH\textsubscript{2}), 63.5 ppm (d, 13C CH\textsubscript{2}) = 4.7 Hz, 3H, (CH\textsubscript{3}NCH\textsubscript{3}), 78.6 ppm (13C CH\textsubscript{2}) = 13.1 Hz, CH\textsubscript{2}), 110 ppm (121.5 MHz, CD\textsubscript{3}Cl\textsubscript{2}), \( \Pi = 39.2 \) ppm (d, \( J_{\text{HH}} = 138 \) Hz); Rh NMR (12.6 MHz, CD\textsubscript{3}Cl\textsubscript{2}); \( \Pi = 1272 \) ppm (d, \( J_{\text{HH}} = 138 \) Hz); HRMS (MALDI); m/z: 776.1975 (calcd for C\textsubscript{61}H\textsubscript{49}N\textsubscript{2}P\textsubscript{3}Rh\textsubscript{5}Cl\textsubscript{2}); 776.1948 (calcld for C\textsubscript{61}H\textsubscript{49}N\textsubscript{2}P\textsubscript{3}Rh\textsubscript{5}Cl\textsubscript{2}).

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Keywords: density functional calculations · EPR spectroscopy · heterocycles · redox chemistry · rhodium
The decomposition of A. Schweiger, G. Jeschke, CoNC heterocycles: a) R. Dreos, A. Felluga, G. Nardin, L. For comparison, the neutral pentacoordinate 18-electron complex 

See, for example: S. Hollenstein, T. Laube, V. M. RayDCN4Hn, crystals, orthorhombic, space group Pnma, c = 13.634(1), V = 4173(3) Å³, Z = 4, R_{1} = 0.0598, wR_2 = 0.0711, direct methods, refinement against full matrix (versus $F^2$) with SHELXTL (version 6.12) and SHELXL-97, 341 parameters, calcd, but the distortions are much smaller: e) R. Schmid, Turner, J. Am. Chem. Soc. 2005, 127, 1895; D. G. H. Hetterscheid, M. Bens, B. de Bruin, Dalton Trans. 2005, 5, 979.

Formally, 6 could be described as a RhI complex, but the values of such complexes are significantly different: K. K. Pandey, Coord. Chem. Rev. 1992, 121, 1.

The classical way to influence the redox potential of a transition-metal complex is to destabilize the ground-state structure of one partner in a redox couple. For examples of this strategy, see: a) C. O. Dietrich-Buchecker, J. Guilleum, J.-M. Kern, C. Pascard, C. Pflug, A. Bertuleit, G. Kehr, R. FrDCN4Mhlich, G. Erker, J. Magn. Reson. 1978, 30, 577.


The decomposition of 6 gives about 20% [Rh(trop2NMe)2(PPh3)]OTf (3) and three other rhodium phosphate complexes of unknown structure.

The poor resolution is probably a result of considerable spatial localization and poor glass formation in frozen solution.

DFT calculations were performed with the Amsterdam Density Functional (ADF 2005.01) package. Details are given in the Supporting Information.


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The poor resolution is probably a result of considerable g strain caused by a distribution of different molecular conformations and poor glass formation in frozen solution.

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