Communications

Carbene Transfer between Transition-Metal Ions

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Summary: A carbene transfer reaction between transition-metal complexes is reported. Carbene complexes of Pd(II), Pt(II), Rh(I), and Au(I) are formed via the reaction of (CO)2M═CN(R)CH2CH2N(R) (M = W, Mo, Cr; R = Et, allyl) with (PhCN)2PdCl2, (PhCN)2PtCl2, [(CO)2RhCl]2, and (Me2S)AuCl. The complexes [ClPd═CN(Et)CH2CH2N(Et)]2, Cl2Pd═CN(allyl)CH2CH2N(allyl)], cis-(CO)2ClPt═CN(Et)CH2CH2N(Et), cis-Cl2Pt═CN(R)CH2CH2N(R)], (CO)2ClRh═CN(Et)CH2CH2N(Et)], and (Au═CN(Et)CH2CH2N(Et)]2Cl are prepared in high yields via a carbene transfer pathway. The X-ray structures of [ClPd═CN(Et)CH2CH2N(Et)]2 (4) and cis-(CO)2ClPt═CN(Et)CH2CH2N(Et) (5) are reported.

Diaminocarbenes, or "bottleable carbenes", have received considerable attention because they can be isolated and structurally characterized as free carbenes.1-4 The electronic influence of the diamino groups is believed to be responsible for the carbene's stability as well as its nucleophilic character. Accordingly, these carbenes are good donors toward various metal ions.5,6 An interesting example reported by Herrmann and co-workers6 is bis(3,4,5-tetramethylimidazol-2-ylidene)palladium(II) iodide, which functions as a catalyst for the Heck reaction under extreme conditions.

Transition metal complex mediated carbene transfer reactions are important tools for organic synthesis, but the simple transfer of carbene ligands between metal ions is rare.7,8 Since diaminocarbene can act as a donor ligand, transfer between metal ions is amenable to study. In a previous investigation, we were able to...
prepare the cyclic diamino-substituted carbene complexes 1 via the reaction of W(CO)_6 with the amine-

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\begin{align*}
1a & : R = \text{CH}_2\text{CH}_2\text{N}=	ext{CH}_2, \\
1b & : R = \text{CH}_2\text{CH}_2\text{N}=	ext{CH}_2.
\end{align*}
\]

phosphinimine H_2NCH_2CH_2N=PPh_3 followed by alkylation.\(^9\) Herein we report that the dianionicarbin in 1 can be transferred to other metals.

The first indication of carbene transfer came from the reaction of 1b with 0.5 mol equiv of (PhCN)_2PdCl_2 in dichloromethane at room temperature for 0.5 h.\(^10\) During the reaction period, carbon monoxide gas evolved and a dark-colored material precipitated from the reaction, which was identified as a mixture of tungsten complexes originating from the decomposition of the W(CO)_6 fragment. Diamino carbene ligands were transferred from the tungsten metal to the palladium center to form the bis(carbene) complex 2 in 92% isolated yield, which then isomerized to the more stable cis isomer 3 upon standing in solution.\(^11\)

When the N-substituent was an ethyl group as in 1a, reaction with an equimolar amount of (PhCN)_2PdCl_2 resulted in the formation of the chloride-bridged dimer 4 in 84% yield (Figure 1). Although complex 2 formed within a few minutes at room temperature, complex 4 required several hours of refluxing in chloroform for complete conversion. This suggests that N-coordination of the carbon-carbon double bond to the palladium metal ion plays a role in both the rate of carbene transfer and the structure of the product. The palladium carbene complexes are stable solids and were characterized by analytical and spectroscopic means. In addition, the structure of 4 was confirmed by a X-ray single-crystal determination.\(^12\)

Investigation of the carbene transfer reaction with other transition-metal complexes was also conducted. Reaction of 1a with (PhCN)_2PtCl_2 in dichloromethane at room temperature for 48 h produced the carbene complex 5 in 93% yield,\(^13\) which shows that both carbene and carbonyl ligands had been transferred. Carbonyl ligand transfer to the platinum and not the palladium may be due to the stability of the expected complexes. To our knowledge, such a synthetic route to a platinum carbene complex is unprecedented. The X-ray crystal structure of 5 is illustrated in Figure 2. Both the bond distances Pt–C(2) (2.011(1) Å) and Pt–C(1) (1.841(1) Å) are typical for such ligands. The infrared carbonyl absorption of stretching appears at 2104 cm\(^{-1}\),

**Table 1.** Bond distances (Å) and angles (deg) for complex 4.

<table>
<thead>
<tr>
<th>Bond Distances</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–C(1)</td>
<td>1.84(1)</td>
</tr>
<tr>
<td>Pt–C(2)</td>
<td>1.94(1)</td>
</tr>
<tr>
<td>Pt–C(3)</td>
<td>1.95(1)</td>
</tr>
</tbody>
</table>

**Table 2.** Bond distances (Å) and angles (deg) for complex 5.

<table>
<thead>
<tr>
<th>Bond Distances</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–C(1)</td>
<td>1.84(1)</td>
</tr>
<tr>
<td>Pt–C(2)</td>
<td>1.95(1)</td>
</tr>
<tr>
<td>Pt–C(3)</td>
<td>1.96(1)</td>
</tr>
</tbody>
</table>

**Table 3.** Crystal data for complexes 4 and 5.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
<th>C (mol%)</th>
<th>H (mol%)</th>
<th>N (mol%)</th>
<th>Found: C (mol%)</th>
<th>Found: H (mol%)</th>
<th>Found: N (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C_8H_14ON_2Cl_2Pt</td>
<td>22.87%</td>
<td>3.43%</td>
<td>6.67%</td>
<td>23.07%</td>
<td>3.43%</td>
<td>6.67%</td>
</tr>
<tr>
<td>5</td>
<td>C_8H_14ON_2Cl_2Pt</td>
<td>22.87%</td>
<td>3.43%</td>
<td>6.67%</td>
<td>23.07%</td>
<td>3.43%</td>
<td>6.67%</td>
</tr>
</tbody>
</table>

**Figure 1.** Structure of complex 4. Bond distances (Å) and angles (deg): Pt–C(1), 1.946(3); C(1)–N(1), 1.317(5); Pt–C(1), 2.248(1); N1–C1–Pd, 124.3(3); Cl(1)–Pd–Cl(1), 177.1(1).

**Figure 2.** ORTEP view of 5. Bond distances (Å) and angles (deg): Pt–C(1), 1.841(1); Pt–C(2), 2.011(1); C(1)–O, 1.12(2); C(1)–Pt–C(2), 91.3(5); Pt–C(1)–O, 179(1).
which is essentially identical with that in cis-(PET3)Pt-(CO)Cl2 (2105 cm<sup>-1</sup>).<sup>14</sup> This implies that the electronic donating ability of the diaminocarbene ligands is similar to that of a trialkylphosphine.<sup>6c</sup>

Treatment of 5 with Me3NO resulted in the formation of the bis(carbene) complex 6a.<sup>15</sup> It appears that a disproportionation reaction took place to form the more stable bis(carbene) complex, although under reflux conditions the platinum bis(carbene) platinum compound 6b was obtained directly from the reaction of 1b with (PhCN)2PtCl2 without the formation of a platinum carbonyl carbene intermediate.

The products formed with the palladium and platinum reactions provide evidence that π-bonding substituents on the carbene N atoms as well as the carbonyl ligand assist the carbene transfer reaction. Chromium and molybdenum analogues of 1 undergo the carbene transfer reaction with platinum and palladium. In addition, Rh(I) and Au(I) carbene complexes 7 and 8 result from the reaction of 1a with [Rh(CO)2Cl]<sub>2</sub> and (Me2S)AuCl, respectively.<sup>16</sup> These Rh(I) and Au(I) carbene complexes are essentially the same as ones previously reported.<sup>17</sup>

We are currently working on developing this chemistry as a route to generate other transition-metal carbene complexes. With sufficient information, it might be possible to determine the mechanism of these reactions.

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**Supporting Information Available:** A complete description of the X-ray crystallographic structure determination of 4 and 5, including tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles, and text giving experimental procedures (10 pages). Ordering information is given on any current masthead page.

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(15) 6a: <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.04 (q, <sup>3</sup>J<sub>Pt-C</sub> = 7.2 Hz, 8 H), 3.57 (s, 8 H), 1.31 (t, <sup>3</sup>J<sub>Pt-C</sub> = 7.2 Hz, 12 H); <sup>13</sup>C NMR δ 194.2 (Pt=C), 47.8 (δ<sup>3</sup>J<sub>Pt-C</sub> = 25.5 Hz), 43.7 (δ<sup>1</sup>J<sub>Pt-C</sub> = 18 Hz), 13.4. Anal. Calc'd for C<sub>14</sub>H<sub>28</sub>N<sub>4</sub>Cl<sub>2</sub>Pt: C, 32.44; H, 5.44; N, 10.81. Found: C, 32.73; H, 5.19; N, 10.60. 6b: yellow solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 5.67–5.52 (m, 4 H), 4.84 (m, 4 H), 4.47 (m, 4 H), 4.05–3.80 (br m, 8 H), 3.67 (s, 8 H);<sup>13</sup>C NMR δ 168.2 (δ<sup>3</sup>J<sub>Rh-C</sub> = 1230 Hz, Pt=C), 131.9, 129.0, 50.3, 48.6 (δ<sup>1</sup>J<sub>Rh-C</sub> = 35 Hz). Anal. Calc'd for C<sub>18</sub>H<sub>28</sub>N<sub>4</sub>Cl<sub>2</sub>Pt: C, 38.17; H, 4.98; N, 9.89. Found: C, 38.45; H, 4.78; N, 9.58.

(16) 7: yellow solid; mp 119–121 °C dec; IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>CO</sub> 2104 cm<sup>-1</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 4.19 (br, 4 H), 3.83 (br, 4 H), 3.55 (s, 8 H), 1.23 (t, <sup>3</sup>J<sub>Ph-CN</sub> = 7.2 Hz, 12 H);<sup>13</sup>C NMR δ 211.8 (d, <sup>1</sup>J<sub>Rh-C</sub> = 36.9 Hz), 187.2 (d, <sup>3</sup>J<sub>Rh-C</sub> = 83.1 Hz), 47.7, 44.8, 13.2. 8: yellow liquid; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 3.75 (s, 8 H), 3.58 (q, <sup>3</sup>J<sub>Ph-CN</sub> = 7.3 Hz, 8 H), 1.31 (t, <sup>3</sup>J<sub>Ph-CN</sub> = 7.3 Hz, 12 H);<sup>13</sup>C NMR δ 203.8 (Au=C), 48.6, 44.9, 14.0. Anal. Calc'd for C<sub>14</sub>H<sub>28</sub>N<sub>4</sub>Cl<sub>2</sub>Au: C, 31.28; H, 6.12; N, 12.16. Found: C, 31.49; H, 5.87; N, 12.46.