



## Simple Synthesis of an Allenylidene Heptavalent Rhenium( $d^0$ ) Complex

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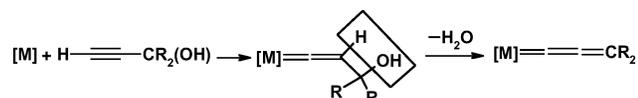
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The first stable transition metal allenylidene complexes were synthesized and characterized by E. O. Fischer<sup>1</sup> and H. Berke<sup>2</sup> in 1976. Since then, transition metal allenylidene complexes have attracted a great deal of attention in organometallic chemistry as a novel class of compounds,<sup>3,4</sup> as precursors of new carbene complexes,<sup>5</sup> as metal-containing polymers,<sup>6,7</sup> and as intermediates for organic synthesis.<sup>8</sup>

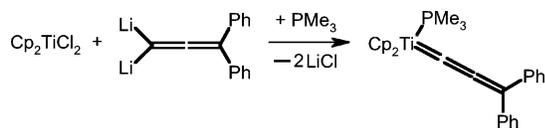
Generally, there are two methods for synthesis of transition metal allenylidene complex. In 1982, Selegue<sup>9</sup> first illustrated that propargyl alcohols  $\text{HC}\equiv\text{C}-\text{C}(\text{RR}')\text{OH}$  can be smoothly converted into a  $\text{C}=\text{C}=\text{CRR}'$  unit in the coordination sphere of an electron-rich transition metal center by elimination of water (Scheme 1).

Scheme 1



Since then, a variety of metal allenylidene complexes have been prepared.<sup>10</sup> Most known transition metal allenylidene complexes have  $d^6$  or  $d^8$  electron configuration, while high-valent  $d^0$  transition metal allenylidene complexes are rare. The first  $d^0$  allenylidene complex, a carben titanocene compound, was synthesized by P. Binger and co-workers in 1990.<sup>11</sup> They selected a dilithiodiphenyllene as a reagent for the synthesis of the complex (Scheme 2).

Scheme 2

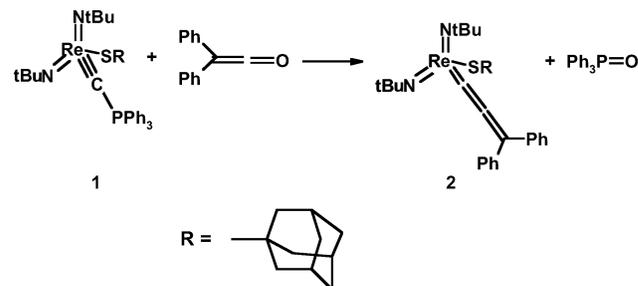


This paper reports a simple way to synthesize an allenylidene rhenium(VII) complex. In comparison to the methods of Selegue<sup>9</sup> and Binger,<sup>11</sup> the diimido adamantyl-thiolato allenylidene rhenium(VII) complex **2** was obtained through a new synthetic strategy, a metathetical reaction of phosphonioalkylidene rhenium complex **1** with diphenylketene (Scheme 3). Complex **1**<sup>12a</sup> was prepared through one-pot reaction of  $\text{Re}(\text{NtBu})_2\text{Cl}_3$ ,  $(\text{Ph}_3\text{PCH}_3)(\text{S}-\text{C}_{10}\text{H}_{15})$  and  $\text{Ph}_3\text{P}=\text{CH}_2$ . Recently, we reported the synthesis of the first tungsten(VI)-phosphonoi-alkylidene complex.<sup>13</sup>

Complex **2** was isolated as a red solid with repeated recrystallization in pentane and characterized by elemental analysis and IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopy.<sup>12b</sup>

The single crystals of complex **2** were obtained as red needles at 4 °C from pentane. The structure was determined by X-ray diffraction.<sup>14</sup> A view of the molecular geometry is shown in Figure 1 with selected bond distances and angles. The geometry around the rhenium center is close to tetrahedral. The angles S1–Re–N1, N1–Re–N2, N1–Re–C1, N2–Re–C1, N2–Re–S1, and S1–

Scheme 3



Re–C1 are 111.8, 121.2, 107.1, 107.3, 109.6, and 97.0°, respectively. The diphenylallenylidene ligand is bound to the metal in a nearly linear fashion, with Re–C1–C2 and C1–C2–C3 angles of 171.4 and 177.0°, respectively. The Re–C1 bond length of 1.898 Å is identical with that found in the other allenylidene complexes

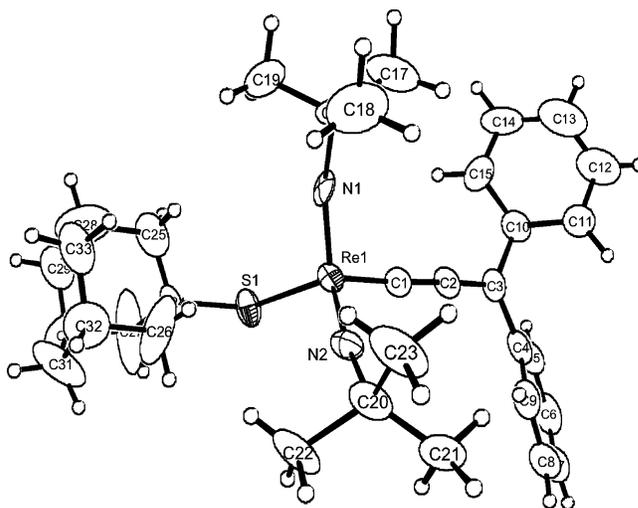
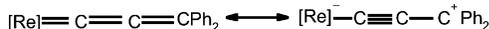


Figure 1. Molecular structure of **2**. Selected bond distances (Å) and angles (deg): Re1–N1, 1.751(9), Re1–N2 1.690(9), Re1–C1 1.898(13), Re1–S1 2.328(3), S1–C24 1.852(11), N1–C16 1.448(13), N2–C20 1.492(14), C1–C2 1.275(16), C2–C3 1.339(15), C3–C4 1.476(16), C3–C10 1.488(16), C4–C5 1.397(16), N2–Re–N1 121.2(4), N2–Re–C1 107.3(5), N1–Re–C1 107.1(5), N2–Re–S1 109.6(3), N1–Re–S1 111.8(3), C1–Re–S1 97.0(4), C24–S1–Re 109.5(3), C16–N1–Re 164.4(8), C20–N2–Re 167.7(8), C2–C1–Re 171.4(10), C1–C2–C3 177.0(12), C2–C3–C4 118.0(11), C2–C3–C10 118.5(10).

(for Cr, 1.99–2.02 Å; for Ru, 1.84–2.00 Å).<sup>3a</sup> In the three-carbon chain, the C1–C2 and C2–C3 distances are 1.275 and 1.339 Å, respectively, which compare well with the other data found in the allenylidene complexes. However, the C1–C2 bond is shorter than the bond length expected for a carbon–carbon double bond (1.30 Å).<sup>15</sup> This result can be explained through the contribution of the resonance form (Scheme 4) of  $[\text{Re}^-]-\text{C}\equiv\text{C}-\text{C}^+\text{Ph}_2$  in the structure of complex **2**.

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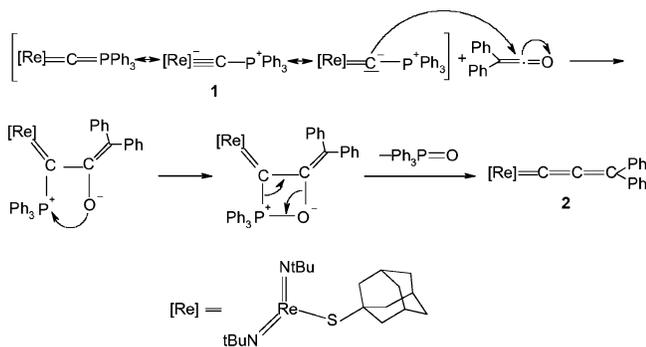
## Scheme 4



A similar conclusion has been reached in the structural analysis of the other allenylidene complexes.<sup>16,17</sup> In the IR spectrum, the very weak band at 1810 cm<sup>-1</sup> is characteristic of the C=C=C unit. Singlets at 235.6, 188.8, and 121.4 ppm in the <sup>13</sup>C NMR spectrum correspond to the C1, C2, and C3 atoms. H. Werner et al. reported similar chemical shifts at about 250, 220, and 150 ppm in the allenylidene complexes [RhCl(=C=C=CRR')(PiPr<sub>3</sub>)<sub>2</sub>] with different substituents.<sup>18</sup>

According to the resonance structure of complex **1** (Scheme 5), the carbon atom with a negative charge is the nucleophilic center, which can attack the carbonyl group of the ketene. Therefore, a phosphor betaine is formed. It is not stable and quickly transforms into a neutral heterocyclic intermediate, which contains phosphorus and oxygen in the ring. This four-member ring intermediate decomposes into allenylidene complex **2** and triphenylphosphine oxide. The first instance of a Wittig-like reaction by a ylide on a transition metal-coordinated carbonyl group was reported by W. C. Kaska.<sup>19</sup> Triphenylphosphine oxide, a typical Wittig reaction product, was isolated from the reaction mixture.

## Scheme 5. Proposed Mechanism for the Formation of Complex 2



Complex **2** in the solid state is stable in the air; it can be kept more than one month. It melts at 136 °C under an inert gas atmosphere.

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**Supporting Information Available:** Tables of crystallographic data collection and refinement parameters, position and thermal parameters, and bond distances and angles for complex **2** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Huttner, G. *Angew. Chem.* **1976**, *88*, 683–684; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623–624.
- Berke, H. *Angew. Chem.* **1976**, *88*, 684–685; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624–625.
- (a) Bruce, M. I.; *Chem. Rev.* **1998**, *98*, 2797–2858. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59–128. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197–257.
- Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–406.
- Pilette, D.; Ouzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809.
- (a) Macomber, D.; Hung, M. H.; Liang, M.; Verma, A. G.; Madhukar, P. *Macromolecules* **1988**, *21*, 1187. (b) Hagihara, N.; Songashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149. (c) Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci.: Polym. Chem. Ed. Engl.* **1980**, *18*, 349–361.
- (a) Schrock, R. R.; Luo, S.; Lee, J. C.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883–3895. (b) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131–12132. (c) Mizumoto, T.; Masuda, T.; Higashimura, T. *Macromol. Chem. Phys.* **1995**, *196*, 1769–1771.
- Schubert, U., Ed. *Advances in Metal Carbene Chemistry*; Kluwer Academic: Dordrecht, 1989.
- Selegue, J. P. *Organometallics* **1982**, *1*, 217–218.
- (a) Crochet, P.; Esteruelas, M. A.; Lopez, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479–3486. (b) Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49–62. (c) Piro, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *462*, C18–C20. (d) Matsuzaka, H.; Koizumi, H.; Takagi, Y.; Nishio, M.; Hida, M. *J. Am. Chem. Soc.* **1993**, *115*, 10396–10397. (e) Matsuzaka, H.; Takagi, Y.; Haidi, M. *Organometallics* **1994**, *13*, 13–15. (f) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921–5923. (g) Touchard, D.; Guesmi, S.; Bouchaib, M.; Haquette, P.; Daridor, A.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2579–2581.
- Binger, P.; Müller, P.; Wenz, R.; Mynott, R. *Angew. Chem.* **1990**, *102*, 1070; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1037–1038.
- (a) **1**: 3.57 g (8.03 mmol) of [Ph<sub>3</sub>P–CH<sub>2</sub>][S–C<sub>10</sub>H<sub>15</sub>] in 10 mL of THF was dropwise added with stirring to a solution of 2.99 g (6.88 mmol) of Re(NtBu)<sub>2</sub>Cl<sub>3</sub> in 20 mL of THF at –80 °C. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm slowly to ambient temperature and stirred for 2 h. During this period, the reaction solution turned dark red in color. Then, a solution of 5.90 g (21.32 mmol) of Ph<sub>3</sub>P=CH<sub>2</sub> in 30 mL THF was added over 20 min to this mixture at –80 °C. A white flocculent precipitate was formed. The suspension was slowly heated to room temperature over 20 min, stirred for 2 h, and then filtered. The filtrate was dried with pump. The red residue was extracted with a mixture of 5 mL of toluene and 30 mL of pentane to give the analytically pure solid at –30 °C in a refrigerator: (3.8 g, 72%) mp 117–119 °C (dec). Elemental analysis C<sub>37</sub>H<sub>48</sub>N<sub>2</sub>PSRe (%): calcd C 57.71, H 6.28, N 3.65; found C 57.32, H 6.53, N 3.84. <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 293K): δ = 1.49 (s, 18 H, NC(CH<sub>3</sub>)<sub>3</sub>), 1.59–2.33 (15H, adamantyl-*H*), 7.02 and 7.75 (m, 15H, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz): δ = 31.46 (s, S–CH<sub>2</sub>), 32.33 (s, NC(CH<sub>3</sub>)<sub>3</sub>), 36.89 (s, S–CH<sub>2</sub>), 43.54 (s, S–C), 47.91 (s, S–CH), 67.95 (s, NC(CH<sub>3</sub>)<sub>3</sub>), 129.82 (d, <sup>1</sup>J(PC) = 88.54 Hz, PPh–C<sub>ipso</sub>), 128.69 (d, <sup>3</sup>J(PC) = 12.2 Hz, PPh–C<sub>meta</sub>), 133.48 (d, <sup>2</sup>J(PC) = 9.76 Hz, PPh–C<sub>ortho</sub>), 131.58 (d, <sup>4</sup>J(PC) = 2.5 Hz, PPh–C<sub>para</sub>), 255.82 (d, <sup>1</sup>J(PC) = 11.0 Hz, Re=C=P) ppm. <sup>31</sup>P NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 10.8 (s, ReCP), (s). (b) **2**: 300 mg (1.54 mmol) of diphenylketene was added to a solution of complex **1** (0.90 g, 1.16 mmol) in 40 mL of toluene at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. Volatiles were removed in a vacuum, and the residue was extracted with pentane (2 × 80 mL) to give a mixture of complex **2** and Ph<sub>3</sub>P=O. Repeated recrystallization from pentane at 4 °C yielded red single crystals suitable for X-ray structure analysis: 290 mg (36%); mp 136–138 °C (dec). Elemental analysis C<sub>33</sub>H<sub>43</sub>N<sub>2</sub>SRe (%): calcd C 57.78, H 6.32, N 4.08; found C 57.80, H 6.34, N 4.12. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 293K): δ = 1.50 (s, 18 H, NC(CH<sub>3</sub>)<sub>3</sub>), 1.72–2.36 (15H, adamantyl-*H*), 7.05–7.88 (m, 10 H, CH<sub>arom</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz): δ = 31.50 (s, NC(CH<sub>3</sub>)<sub>3</sub>), 32.28 (s, S–CH<sub>2</sub>), 48.28 (s), 65.62 (s), 43.94 (s), 45.68 (s), 71.20 (s, NC(CH<sub>3</sub>)<sub>3</sub>), 121.42 (s, Re=C=C=CPh<sub>2</sub>), 188.77 (s, Re=C=C=CPh<sub>2</sub>), 235.56 (s, Re=C=C=CPh<sub>2</sub>), 128.82 (s), 130.69 (s), 131.28 (s), 132.18 (s), 135.74 (s).
- Li, X.; Schopf, M.; Stephan, J.; Harms, K.; Sundermeyer, J. *Organometallics* **2002**, *21*, 2356–2358.
- For the crystal structure of complex **2**, see Supporting Information.
- Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.
- Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Gonzalez-Cueva, M.; Lastra, E.; Borge, J.; Garcia-Granda, S.; Perez-Carreño, E. *Organometallics* **1996**, *15*, 2137–2147.
- Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373–381.
- Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721–2727.
- (a) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F.; Korte, W. D. *J. Am. Chem. Soc.* **1974**, *96*, 2847–2854. (b) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F. *J. Organomet. Chem.* **1973**, *47*, 391–402. (c) Kaska, W. C.; Mitchell, D. K.; Korte, W. D. *J. Chem. Soc., Chem. Commun.* **1970**, 1384–1385.

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