Metallacycles

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Synthesis and Characterization of a Rhenabenzyne Complex**

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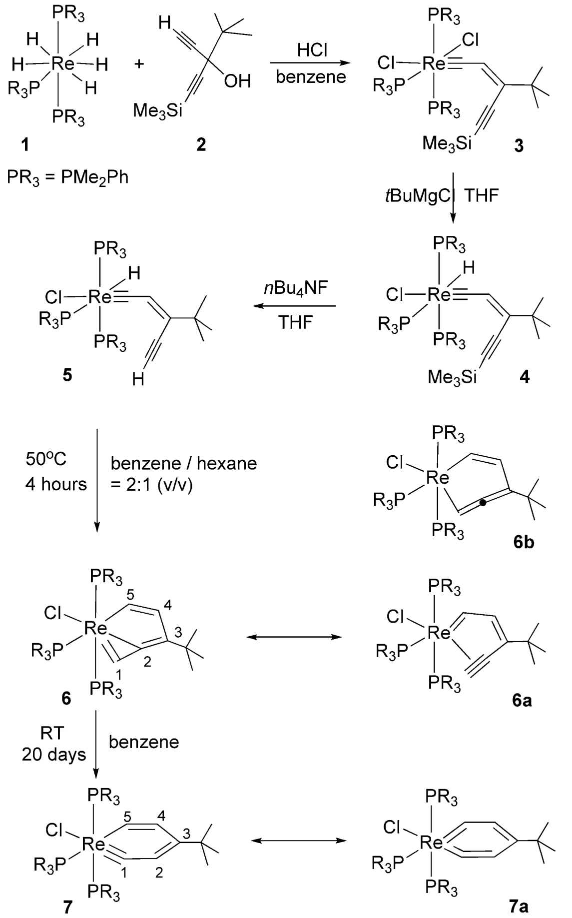
There has been much interest in the chemistry of transition-metal-containing metallaaromatic compounds. In particular metallabenzenes, which are organometallic compounds derived by the formal replacement of a C–H group in benzene with an isolobal transition metal fragment, have attracted considerable attention.[1] Previous studies have led to the isolation and characterization of an impressive number of stable metallabenzenes, especially those of osmium,[2–4] iridium,[5–8] platinum,[9] ruthenium,[10,11] and rhenium.[12]

Metallabenzynes,[13] which are organometallic compounds derived from formal replacement of a carbon atom or a C–H group in benzyne with an isolobal transition metal fragment, are closely related to metallabenzenes. At first sight, one might expect that metallabenzynes may be too unstable to be isolated, because organic compounds with a C≡C bond in the six-membered ring, for example, benzyne and cyclohexyne, are thermally highly unstable because of ring strain. Nevertheless, in recent years, several stable osmabenzynes have been isolated[14] and their interesting chemical properties have been demonstrated. For example, osmabenzynes, such as metallabenzenes and aromatic compounds, can undergo electrophilic substitution reactions.[14b]

Compared with the chemistry of metallabenzenes, that of metallabenzynes is much less developed. For instance, while stable metallabenzenes with several metals are known, to date, isolated metallabenzynes are limited to those containing an osmium center. The synthesis and characterization of metallabenzynes with metals other than osmium remain important goals in the development of the chemistry of these compounds. Herein, we report the preparation and structural characterization of the first stable rhenabenzyne complex.

The rhenabenzyne complex was synthesized by the synthetic route outlined in Scheme 1. Reaction of $[ReH_5(PMe_2Ph)_3]$ (**1**) with alkynol **2** in the presence of HCl produced the dichlorocarbyne complex **3**. Treatment of **3** with *tert*-butylmagnesium chloride produced the hydridochlorocarbyne complex **4**, likely through the intermediate $[Re(\equiv C\text{-}CH{=}C(tBu)C{\equiv}CSiMe_3)Cl(tBu)(PMe_2Ph)_3]$, which underwent β-H elimination. Experimentally, the side product $CH_2{=}CMe_2$ has indeed been detected by in situ ^1H NMR spectroscopy. Complex **4** was isolated as a blue solid in 63 % yield, and could be stored under nitrogen at room temperature for a week without appreciable decomposition. The Me_3Si group in **4** could be easily removed by treatment of **4** with nBu_4NF to give carbyne complex **5**. The new carbyne complexes **3**–**5** can be readily identified by NMR spectroscopy. For example, the ^1H NMR spectrum of **5** shows the Re–H signal at 1.85 ppm as a doublet of triplets with P–H coupling constants of 50.0 and 28.0 Hz, the Re≡CCH signal at 4.42 ppm, and the C≡CH signal at 3.22 ppm; the $^{13}C\{^1H\}$ NMR spectrum of **5** shows the Re≡C signal at 254.1 ppm and the C≡CH signals at 88.4 and 83.8 ppm.



Scheme 1. Preparation of rhenabicyclo[3.1.0]hexatriene **6** and rhenabenzyne **7**.

In the solid state, complex **5** can be stored under nitrogen for at least three days without any decomposition, however, it is thermally unstable in solution. When a solution of **5** in benzene was stored at room temperature for three days, complex **5** completely rearranged to form complex **6**. The rearrangement reaction was complete within 4 h when a solution of **5** in benzene/hexane was heated at 50 °C. Complex

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6 could be isolated as a red solid in 74 % yield. In the solid state, complex **6** remained unchanged when it was stored under nitrogen for several days. When a solution of **6** in benzene was stored for 20 days at room temperature, complex **6** completely rearranged to complex **7**.

The structure of complex **6** has been confirmed by an X-ray diffraction study,[15] and contains an essentially planar bicyclic metallacycle (Figure 1). The maximum deviation from the least-squares plane through Re1 and C1–C5 is 0.028 Å for C1. The C1–C2, C2–C3, C3–C4, and C4–C5 bond lengths are 1.310(11), 1.337(11), 1.426(12), and 1.350(14) Å, respectively. The Re–C1 bond length of 1.933(7) Å is within the range of those reported for typical Re=CHR(carbene) bonds (1.850–2.143 Å),[16,17] and shorter than those reported for typical Re–C(vinyl) bonds (1.996–2.305 Å).[16,18] The Re–C5 bond length of 2.158(8) Å is within the range of those reported for typical Re–C(vinyl) bonds,[16,18] and longer than those reported for typical Re=CHR(carbene) bonds.[16,17] Our preliminary DFT calculations show that the optimized structure agrees well with the structural features of **6** described above (see the Supporting Information for details).

Scheme 1 shows two resonance forms that contribute to the overall structure of the metallacycle of complex **6**: metallabicyclo[3.1.0]hexatriene complex **6** and alkyne–carbene complex **6a**.[19] The structural feature suggests that either one of the two resonance forms alone cannot properly describe the molecular structure. The resonance form **6** can account for the bond lengths of the Re–C1, Re–C2, Re–C5, C2–C3, C3–C4, and C4–C5 bonds, but cannot adequately account for the fact that C1–C2 is even shorter than C2–C3 and that the C1-C2-C3 moiety is almost linear. The shorter C1–C2 bond and the almost linear C1-C2-C3 moiety can be related to the contribution from the resonance form **6a**. Alternatively, one might consider **6b** (see Scheme 1), in which C1, C2, and C3 are part of an allenyl ligand, as a possible resonance form that contributes to the overall structure to give the shorter C1–C2 bond and the almost linear C1-C2-C3 moiety. We know that the four substituents on an allene moiety in the ground state are not in the same plane. As the atoms bonded to C1 and C3 in complex **6** are nearly coplanar, **6b** cannot be a stable resonance form, and is therefore not expected to make a significant contribution to the overall structure. The molecular structure is better described by a resonance hybrid of **6** and **6a** shown in Scheme 1. Natural bond orbital (NBO) analyses suggest that Re–C1 can be considered to have double-bond character, while Re–C5 and Re–C2 have single-bond character. The calculated Wiberg bond indices (bond orders, which are a measure of bond strength) of Re–C1, Re–C2, and Re–C5 are 1.22, 0.70, and 0.91, respectively (see the Supporting Information for the calculated bond indices of the remaining bonds in the metallacycle).

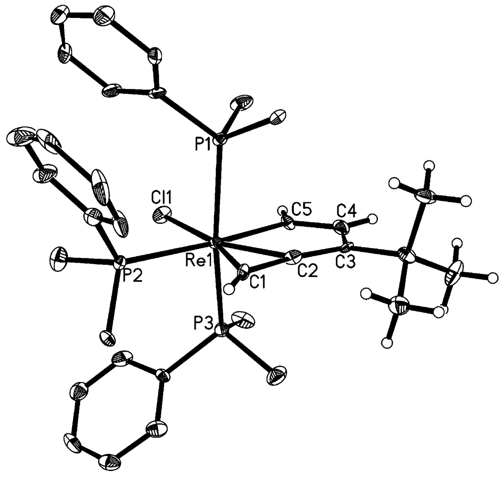

Figure 1. ORTEP drawing of **6** with thermal ellipsoids at 35 % probability level. The hydrogen atoms on PMe_2Ph ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re1–C1 1.933(7), Re1–C2 2.104(8), Re1–C5 2.158(8), C1–C2 1.310(11), C2–C3 1.337(11), C3–C4 1.426(12), C4–C5 1.350(13); C1-Re1-C2 37.6(3), C1-Re1-C5 107.4(3), C2-Re1-C5 69.9(3), C2-C1-Re1 78.3(5), C1-C2-C3 170.0(7), C1-C2-Re1 64.1(4), C3-C2-Re1 125.7(5), C2-C3-C4 109.5(7), C5-C4-C3 115.0(8), C4-C5-Re1 119.9(6).

Consistent with the solid-state structure, the ^{1}H NMR spectrum of **6** showed signals at 8.79, 9.47, and 14.92 ppm for the three protons on C4, C5, and C1 of the metallacycle, respectively. The ^{13}C{^{1}H} NMR spectrum of **6** showed signals at 208.0 (C1), 169.9 (C5), 151.0 (C2), 147.3 (C4), and 132.9 ppm (C3).

Rhenabenzyne **7** has been characterized by NMR spectroscopy, elemental analysis, as well as X-ray diffraction. The ^{1}H NMR spectrum of **7** showed the signals of the three protons on C2, C4, and C5 of the metallacycle at 4.92, 8.06, and 12.28 ppm, respectively. The ^{13}C{^{1}H} NMR spectrum of **7** showed the Re≡C signal at 289.4 ppm. The signal corresponding to the other metal-bound carbon atom (ReC) was observed at 210.4 ppm. With the aid of DEPT135 and ^{1}H–^{13}C HSQC techniques, the ^{13}C signals for the remaining carbon atoms of the metallacycles were located at 173.6, 124.2, and 110.7 ppm, corresponding to C3, C4, and C2, respectively.

The structure of **7** has also been confirmed by X-ray diffraction analysis. As shown in Figure 2, **7** contains an essentially planar six-membered metallacycle. The maximum deviation from the least-squares plane through Re1 and C1-C5 is 0.020 Å for C5. The Re-C1-C2 angle (150.8(3)°) is significantly smaller than that expected for either a carbyne or a vinylidene complex, because of the constraint of the six-membered ring. The C–C distances in the ring in **7** (1.367–1.457 Å) are typical of a regular aromatic system. The Re–C1 bond length (1.774(4) Å) is in the high end of the observed range for typical Re≡C bond lengths (1.672–1.802 Å),[16,20] and shorter than the lengths found for typical Re=C bonds in rhenium vinylidene complexes (1.925–2.046 Å).[16,21] The Re–C5 bond length (2.107(4) Å) is within the range of typical Re–C(vinyl) bond lengths (1.996–2.305 Å),[16,18] and in the high end of the reported range for typical Re=CH(carbene) bonds (1.850–2.143 Å).[16,17] The structural data indicate that the metallacycle of **7** has a delocalized structure with contributions from resonance structures **7** and **7a**, with **7** being more important.

In summary, we have successfully isolated and structurally characterized the first rhenabenzyne complex. We are currently exploring the possibility of isolating metallabenzynes of other middle or early transition metals.

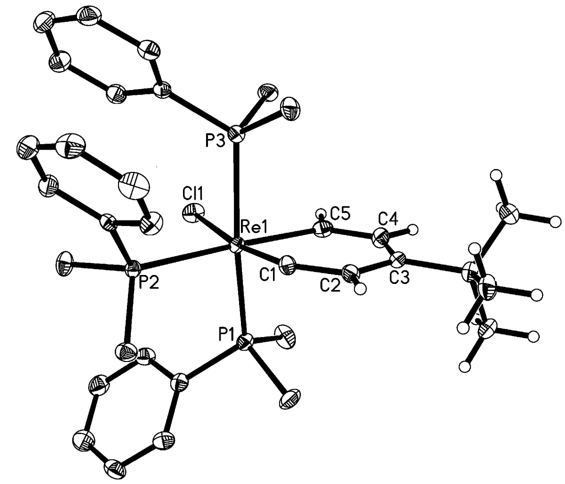

Figure 2. ORTEP drawing of **7** with thermal ellipsoids at 35% probability level. The hydrogen atoms on $\mathrm{PMe_2Ph}$ ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re1–C1 1.774(4), Re1–C5 2.107(4), C1–C2 1.406(5), C2–C3 1.367(6), C3–C4 1.457(6), C4–C5 1.369(6); C1-Re1-C5 79.08(17), C2-C1-Re1 150.8(3), C2-C3-C4 120.6(4), C3-C2-C1 115.4(4), C4-C5-Re1 128.7(3), C5-Re1-Cl1 87.51(11), C5-Re1-P1 84.59(12), C5-Re1-P2 176.89(11), C5-Re1-P3 85.52(11), C5-C4-C3 125.4(4).

Experimental Section

$[\mathrm{Re}(\equiv\mathrm{C{-}CH{=}C}(t\mathrm{Bu})\mathrm{CH{=}CH{-}})\mathrm{Cl}(\mathrm{PMe_2Ph})_3]$ (7): A solution of **6** (433 mg, 0.57 mmol) in benzene (5 mL) was stored at room temperature for 20 days; NMR experiments suggest that **6** was completely converted to **7** after this time. The mixture was stored for additional 20 days to give a crystalline solid together with some oily material. The crude solid was washed with hexane (3 × 3 mL) under sonication, then collected by filtration and dried under vacuum. The crystals (179 mg, 41.3%) were separated by hand with the help of a microscope. An analytically pure sample was obtained by column chromatography on silica gel with benzene as eluent. The blue band was collected, and the solvent was removed completely to give a cadet-blue solid. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.98 MHz, $\mathrm{C_6D_6}$): $\delta = -23.1$ (t, $J(\mathrm{PP}) = 19.9$ Hz), -24.5 ppm (d, $J(\mathrm{PP}) = 20.4$ Hz); $^1\mathrm{H}$ NMR (400.13 MHz, $\mathrm{C_6D_6}$): $\delta = 1.40$ (d, $J(\mathrm{PH}) = 6.8$ Hz, 6H, $\mathrm{P}Me_2\mathrm{Ph}$), 1.40 (t, $J(\mathrm{PH}) = 3.4$ Hz, 6H, $\mathrm{P}Me_2\mathrm{Ph}$), 1.47 (s, 9H, $\mathrm{C(CH_3)_3}$), 1.78 (t, $J(\mathrm{PH}) = 3.8$ Hz, 6H, $\mathrm{P}Me_2\mathrm{Ph}$), 4.92 (dt, $J(\mathrm{PH}) = 4.4$, 2.0 Hz, 1H, $\mathrm{Re{\equiv}C{-}CH}$), 7.00–7.08 (m, 9H, Ph), 7.38–7.46 (m, 4H, Ph), 7.56–7.66 (m, 2H, Ph), 8.06 (ddt, $J(\mathrm{HH}) = 10.7$ Hz, $J(\mathrm{PH}) = 6.1$, 1.9 Hz, 1H, $\mathrm{Re{-}CH{=}C}H$), 12.28 ppm (ddt, $J(\mathrm{HH}) = 10.8$ Hz, $J(\mathrm{PH}) = 7.1$, 1.7 Hz, 1H, $\mathrm{Re{-}CH}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, $\mathrm{C_6D_6}$): $\delta = 289.4$ (dt, $J(\mathrm{PC}) = 12.0$, 11.9 Hz, $\mathrm{Re{\equiv}C}$), 210.4 (dt, $J(\mathrm{PC}) = 46.8$, 12.1 Hz, $\mathrm{Re{-}CH}$), 173.6 (t, $J(\mathrm{PC}) = 3.5$ Hz, $Ct\mathrm{Bu}$), 141.7 (dt, $J(\mathrm{PC}) = 33.6$, 2.2 Hz, Ph), 140.8 (dt, $J(\mathrm{PC}) = 18.9$, 1.6 Hz, Ph), 129.6 (d, $J(\mathrm{PC}) = 10.0$ Hz, Ph), 129.6 (t, $J(\mathrm{PC}) = 4.2$ Hz, Ph), 127.5 (s, Ph), 127.3 (s, Ph), 127.2 (d, $J(\mathrm{PC}) = 7.2$ Hz, Ph), 126.9 (t, $J(\mathrm{PC}) = 4.0$ Hz, Ph), 124.2 (t, $J(\mathrm{PC}) = 2.9$ Hz, $\mathrm{Re{-}CH{=}C}H$), 110.7 (s, $\mathrm{Re{\equiv}C{-}C}H$), 36.3 (s, tBu), 30.0 (s, tBu), 18.3 (d, $J(\mathrm{PC}) = 22.1$ Hz, $\mathrm{P}Me_2\mathrm{Ph}$), 14.6 (dt, $J(\mathrm{PC}) = 1.8$ Hz, 16.7 Hz, $\mathrm{P}Me_2\mathrm{Ph}$), 14.5 ppm (t, $J(\mathrm{PC}) = 16.4$ Hz, $\mathrm{P}Me_2\mathrm{Ph}$); elemental analysis (%) calcd for $\mathrm{C_{33}H_{45}ClP_3Re}$: C 52.41, H 6.00; found: C 52.16, H 6.16.

Crystallographic data for **3**, **6**, and **7**, as well as details for the preparation and characterization of **3–7** can be found in the Supporting Information.

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Keywords: carbynes · metallabenzynes · metallacycles · rhenium · transition metals

[1] For examples, see: a) J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205; b) C. W. Landorf, M. M. Haley, *Angew. Chem.* **2006**, *118*, 4018; *Angew. Chem. Int. Ed.* **2006**, *45*, 3914; c) L. J. Wright, *Dalton Trans.* **2006**, 1821.

[2] a) G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811; b) C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *Angew. Chem.* **2000**, *112*, 766; *Angew. Chem. Int. Ed.* **2000**, *39*, 750; c) C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *J. Organomet. Chem.* **2001**, *623*, 109; d) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2006**, *25*, 1771; e) P. M. Johns, W. R. Roper, S. D. Woodgate, L. J. Wright, *Organometallics* **2010**, *29*, 5358.

[3] a) H. Xia, G. He, H. Zhang, T. B. Wen, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2004**, *126*, 6862; b) L. Gong, Y. Lin, T. B. Wen, H. Zhang, B. Zeng, H. Xia, *Organometallics* **2008**, *27*, 2584; c) B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem.* **2009**, *121*, 5569; *Angew. Chem. Int. Ed.* **2009**, *48*, 5461; d) L. Gong, Z. Chen, Y. Lin, X. He, T. B. Wen, X. Xu, H. Xia, *Chem. Eur. J.* **2009**, *15*, 6258; e) H. Zhang, L. Wu, T. B. Wen, H. Xia, *Chem. Eur. J.* **2009**, *15*, 3546; f) J. Huang, R. Lin, L. Wu, Q. Zhao, C. Zhu, T. B. Wen, H. Xia, *Organometallics* **2010**, *29*, 2916.

[4] a) P. Barrio, M. A. Esteruelas, E. Oñate, *J. Am. Chem. Soc.* **2004**, *126*, 1946; b) Q. Zhao, L. Gong, C. Xu, J. Zhu, X. He, H. Xia, *Angew. Chem.* **2011**, *123*, 1390; *Angew. Chem. Int. Ed.* **2011**, *50*, 1354.

[5] a) G. R. Clark, G. Lu, W. R. Roper, L. J. Wright, *Organometallics* **2007**, *26*, 2167; b) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2008**, *27*, 451; c) A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, *28*, 5536; d) G. R. Clark, P. M. Johns, W. R. Roper, T. Sohnel, L. J. Wright, *Organometallics* **2011**, *30*, 129.

[6] a) R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 2597; b) H. P. Wu, S. Lanza, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 2824; c) R. D. Gilbertson, T. L. S. Lau, S. Lanza, H. P. Wu, T. J. R. Weakley, M. M. Haley, *Organometallics* **2003**, *22*, 3279; d) H. P. Wu, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2005**, *11*, 1191; e) H. P. Wu, D. H. Ess, S. Lanza, T. J. R. Weakley, K. N. Houk, K. K. Baldridge, M. M. Haley, *Organometallics* **2007**, *26*, 3957.

[7] a) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898; b) E. Álvarez, M. Paneque, M. L. Poveda, N. Rendon, *Angew. Chem.* **2006**, *118*, 488; *Angew. Chem. Int. Ed.* **2006**, *45*, 474; c) K. Ilg, M. Paneque, M. L. Poveda, N. Rendon, L. L. Santos, E. Camona, K. Mereiter, *Organometallics* **2006**, *25*, 2230; d) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, L. L. Santos, E. Álvarez, V. Salazar, K. Mereiter, E. Oñate, *Organometallics* **2007**, *26*, 3403; e) M. Paneque, M. L. Poveda, N. Rendón, E. Álvarez, E. Carmona, *Eur. J. Inorg. Chem.* **2007**, 2711; f) C. S. Chin, H. Lee, M. S. Eum, *Organometallics* **2005**, *24*, 4849; g) C. S. Chin, H. Lee, *Chem. Eur. J.* **2004**, *10*, 4518.

[8] a) J. R. Bleeke, Y. F. Xie, W. J. Peng, M. Chiang, *J. Am. Chem. Soc.* **1989**, *111*, 4118; b) J. R. Bleeke, Y. F. Xie, L. Bass, M. Y. Chiang, *J. Am. Chem. Soc.* **1991**, *113*, 4703; c) J. R. Bleeke, R. Behm, *J. Am. Chem. Soc.* **1997**, *119*, 8503; d) J. R. Bleeke, R. Behm, Y. F. Xie, M. Y. Chiang, K. D. Robinson, A. M. Beatty, *Organometallics* **1997**, *16*, 606, and references therein.

[9] a) V. Jacob, T. J. R. Weakley, M. M. Haley, *Angew. Chem.* **2002**, *114*, 3620; *Angew. Chem. Int. Ed.* **2002**, *41*, 3470; b) C. W. Landorf, V. Jacob, T. J. R. Weakley, M. M. Haley, *Organometallics* **2004**, *23*, 1174; c) V. Jacob, C. W. Landorf, L. N. Zakharov, T. J. R. Weakley, M. M. Haley, *Organometallics* **2009**, *28*, 5183.

[10] a) H. Zhang, H. Xia, G. He, T. B. Wen, L. Gong, G. Jia, *Angew. Chem.* **2006**, *118*, 2986; *Angew. Chem. Int. Ed.* **2006**, *45*, 2920; b) H. Zhang, L. Feng, L. Gong, L. Wu, G. He, T. B. Wen, F. Yang, H. Xia, *Organometallics* **2007**, *26*, 2705; c) L. Wu, L. Feng, H. Zhang, Q. Liu, X. He, F. Yang, H. Xia, *J. Org. Chem.* **2008**, *73*, 2883; d) R. Lin, H. Zhang, S. Li, L. Chen, W. Zhang, T. B. Wen, H. Zhang, H. Xia, *Chem. Eur. J.* **2011**, *17*, 2420; e) R. Lin, H. Zhang, S. H. Li, J. . Wang, H. Xia, *Chem. Eur. J.* **2011**, *17*, 4223.

[11] G. R. Clark, T. R. O'Neale, W. R. Roper, D. M. Tonei, L. J. Wright, *Organometallics* **2009**, *28*, 567.

[12] K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2010**, *122*, 2819; *Angew. Chem. Int. Ed.* **2010**, *49*, 2759.

[13] a) W. R. Roper, *Angew. Chem.* **2001**, *113*, 2506; *Angew. Chem. Int. Ed.* **2001**, *40*, 2440; b) G. Jia, *Acc. Chem. Res.* **2004**, *37*, 479; c) G. Jia, *Coord. Chem. Rev.* **2007**, *251*, 2167.

[14] a) T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem.* **2001**, *113*, 2005; *Angew. Chem. Int. Ed.* **2001**, *40*, 1951; b) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 2856; c) W. Y. Hung, J. Zhu, T. B. Wen, K. P. Yu, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2006**, *128*, 13742; d) T. B. Wen, S. M. Ng, W. Y. Hung, Z. Y. Zhou, M. F. Lo, L. Y. Shek, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2003**, *125*, 884; e) G. He, J. Zhu, W. Y. Hung, T. B. Wen, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2007**, *119*, 9223; *Angew. Chem. Int. Ed.* **2007**, *46*, 9065.

[15] Cryallographic data for **3**, **6**, and **7** can be found in the Supporting Information. CCDC 832281 (**3**), 832282 (**6**), and 832283 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] Based on a search of the Cambridge Structural Database, CSD version 5.32 (November 2010).

[17] For recent examples, see: a) Y. Jiang, O. Blaccque, T. Fox, C. M. Frech, H. Berke, *Organometallics* **2009**, *28*, 4670; b) P. R. Elowe, N. M. West, J. A. Labinger, J. E. Bercaw, *Organometallics* **2009**, *28*, 6218.

[18] For recent examples, see: a) M. N. Uddin, M. A. Mottalib, N. Begum, S. Ghosh, A. K. Raha, D. T. Haworth, S. V. Lindeman, T. A. Siddiquee, D. W. Bennett, G. Hogarth, E. Nordlander, S. E. Kabir, *Organometallics* **2009**, *28*, 1514; b) O. V. Ozerov, M. Pink, L. A. Watson, K. G. Caulton, *J. Am. Chem. Soc.* **2004**, *126*, 2105.

[19] For reported alkyne–carbene complexes, see: a) K. P. Wang, S. Y. Yun, D. Lee, D. L. Wink, *J. Am. Chem. Soc.* **2009**, *131*, 15114; b) F. Hohmann, S. Siemoneit, M. Nieger, S. Kotila, K. H. Dötz, *Chem. Eur. J.* **1997**, *3*, 853; c) K. H. Dötz, T. Schafer, F. Kroll, K. Harms, *Angew. Chem.* **1992**, *104*, 1257; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1236; d) K. H. Dötz, S. Siemoneit, F. Hohmann, M. Nieger, *J. Organomet. Chem.* **1997**, *541*, 285; e) H. Strutz, J. C. Dewan, R. R. Schrock, *J. Am. Chem. Soc.* **1985**, *107*, 5999.

[20] For recent examples, see: a) J. Chen, G. He, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Organometallics* **2010**, *29*, 2693; b) O. V. Ozerov, L. A. Watson, M. Pink, K. G. Caulton, *J. Am. Chem. Soc.* **2004**, *126*, 6363; c) O. V. Ozerov, J. C. Huffman, L. A. Watson, K. G. Caulton, *Organometallics* **2003**, *22*, 2539; d) C. P. Casey, S. Kraft, M. Kavana, *Organometallics* **2001**, *20*, 3795.

[21] For examples, see: a) C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, *Organometallics* **1996**, *15*, 3804; b) A. J. L. Pombeiro, S. S. P. R. Almeida, M. F. C. G. Silva, J. C. Jeffrey, R. L. Richards, *J. Chem. Soc. Dalton Trans.* **1989**, 2381; c) D. R. Senn, A. Wong, A. T. Patton, M. Marsi, C. E. Strouse, J. A. Gladysz, *J. Am. Chem. Soc.* **1988**, *110*, 6096.