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Low-Coordinate Complexes

Maximizing Coordinative and Electronic Unsaturation: Three-Coordinate Dicationic Platinum Complexes**

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Isolable low-coordinate transition-metal complexes could embody the synthetic chemist's somewhat discordant ideals of catalysts that are both conveniently handled and highly active.[1] A number of techniques, chief among them the abstraction of halogeno ligands, can be used to prepare low-coordinate, cationic complexes (or related weakly-coordinated solvent-bound or agostic derivatives), thereby also increasing the electrophilicity of the metal center.[2] Such cationic complexes of Pt have been used to great effect in the activation of C−H bonds, particularly of alkanes.[3] However, an important distinction must be made between truly "low-coordinate" complexes with completely free coordination sites, and their solvent-bound or agostic derivatives.

Dicationic complexes of Pd^{II}, generated in situ by halide abstraction, are often used as catalysts for organic transformations; however, these complexes are assumed to use solvent coordination or other means to satisfy their coordinative unsaturation and reach a valence electron (VE) count of 16.[4] Relatively few dicationic complexes of Pt^{II} are known, but as in the case of palladium, these complexes are best thought of as four-coordinate, 16-electron species.[5] Like their monocationic relatives, such dicationic complexes have proven adept at the activation of C−H bonds.[5d] However, to the best of our knowledge, no dicationic complexes of Group 10 (nor Group 8 or 9) metals exist with VE counts lower than 16. The group of Gagné have prepared a dicationic complex in situ that they formulate as $[Pt(ppp)][BF_4]_2$ (ppp = bis(2-diphenylphosphanylethyl)phenylphosphine); however, in the absence of structural authentication it seems unlikely that this complex is truly three-coordinate.[6] Recently a complex of Pt was reported in which a tricationic phosphine ligand was bound to an anionic $[PtCl_3]^-$ fragment.[7] The overall charge on the complex was 2+; however, the Pt center was four-coordinate.

The *trans* influence of boryl, borylene, and base-stabilized borylene ligands has now been extensively documented.[8] We have previously used salts of weakly coordinating anions (WCAs) and the strong *trans* influence of boryl ligands to prepare T-shaped cations of the form *trans*-$[Pt(BXR)(PCy_3)_2][WCA]$ without agostic interactions, that is, with a completely free coordination site.[9] These are examples of three-coordinate, 14-electron Pt^{II} complexes, which were rare at that time. Addition of pyridine bases to these cationic complexes induced migration of the boron-bound halide to the metal, resulting in cationic, base-stabilized borylene complexes of the form *trans*-$[Pt\{=BR(Py)\}X(PCy_3)_2][WCA]$ (Py = substituted pyridine).[9,10] We recognized these cationic complexes as possible routes to currently unknown low-coordinate dicationic complexes of Group 10 metals. Herein we have used a further WCA salt to abstract the remaining bromo ligands of two base-stabilized borylene complexes of Pt^{II}, providing dicationic base-stabilized borylene complexes. To our surprise, the coordination site *trans* to the borylene ligand is completely free of agostic interactions in the solid state, similar to the majority of the structurally characterized cationic boryl complexes of Pt^{II},[9] making these complexes truly three-coordinate. This coordination site, however, is available for coordination by sterically unimposing donors, such as acetonitrile and CO.

The reaction of a colorless solution of *trans*-$[Pt\{=BNMe_2(4\text{-picoline})\}Br(PCy_3)_2][BAr^f_4]$ (**1a**, $Ar^f = 3{,}5\text{-}C_6H_3\text{-}(CF_3)_2$) or a purple solution of *trans*-$[Pt\{=BFc(4\text{-picoline})\}Br(PCy_3)_2][BAr^f_4]$ (**1b**; Fc = ferrocenyl)[9,10] with an excess of $Na[BAr^f_4]$ yields a yellow solution of **2a** or a blue solution of **2b**, respectively, along with colorless precipitates which are filtered off (Scheme 1). Signals in the $^{31}P\{^1H\}$ NMR spectra of the complexes are shifted to higher frequency by about δ = 20 ppm with respect to the precursors, indicating the formation of three-coordinate Pt^{II} bis(phosphine) complexes (**2a**: δ = 42.1 ppm, $^1J_{P\text{-}Pt} = 2441$ Hz; **2b**: 42.9, $^1J_{P\text{-}Pt} = 2519$ Hz). Layering solutions of **2a** or **2b** with hexanes and toluene leads to two-phase systems of accordingly colored, oily products and weakly colored solvents. Both compounds are stable in CH_2Cl_2 solution with rigorous exclusion of water and oxygen, although the Fc-substituted representative is more sensitive than **2a**.

The molecular structure of the dication of **2a** shows a three-coordinate, *trans*-configured platinum complex with a free coordination site *trans* to the base-stabilized borylene moiety (Figure 1). The P1-Pt-P2 angle of 163.64(4)° and the angular sum around the platinum center (359.84°) lie in the range of T-shaped, cationic boryl platinum complexes (157.26(2)–171.84(6)°).[9] The Pt−B distance (198.2(5) pm) in

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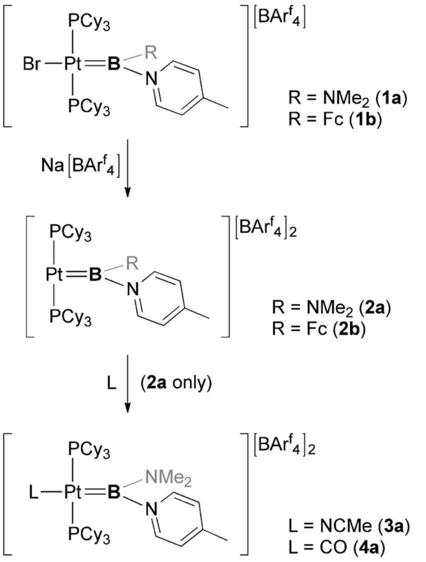

Scheme 1. Synthesis of dications **2**, and reaction of **2a** with the donor ligands acetonitrile and CO. $Ar^f = 3,5\text{-}C_6H_3(CF_3)_2$.

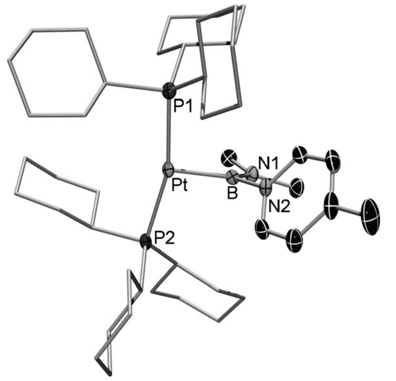

Figure 1. Molecular structure of the dication of **2a** as derived from X-ray crystallography. Ellipsoids set at 50% probability. Hydrogen atoms have been removed for clarity, and cyclohexyl groups have been simplified. Selected bond lengths [pm] and angles [°]: Pt–B 198.2(5), Pt–P1 231.9(1), Pt–P2 233.1(1), B–N1 137.8(7), B–N2 155.1(6); P1-Pt-P2 163.64(4), P1-Pt-B 96.5(1), P2-Pt-B 99.7(1).

2a is about 2% shorter than in its precursor (201.8(4) pm) and compares well with the different distances in *trans*-$[Pt\{B(Br)(NMe_2)\}Br(PCy_3)_2]$ and *trans*-$[Pt\{B(Br)(NMe_2)\}(PCy_3)_2][BAr^f_4]$ (200.9(3) pm and 198.7(4) pm). Here again, the Pt–B distance reflects the boryl character of the base-stabilized borylene moiety. The shortest $Pt–C_{Cy}$ distance of 317.9 pm is out of the range for which agostic interactions in cationic platinum complexes could be inferred.

Fourteen-electron d^8 MXL_2 systems are usually highly reactive and interact even with very weak nucleophiles, such as solvent molecules or weakly coordinating anions,[11] and have agostic C–H interactions.[12] Although quantum-chemical calculations on 14-electron d^8 MXL_2 boryl complexes of the type *trans*-$[Rh(BX_2)(PR_3)_2]$ corroborate that C–H bonds prefer not to coordinate *trans* to the boryl moiety,[13] such an interaction was observed by X-ray crystallography in a 14-electron d^8 MXL_2 PBP-pincer rhodium complex.[14]

The solid-state investigation of a series of cationic boryl–platinum complexes shows no solvent molecules coordinating to the Pt center, and the shortest distances between Pt atoms and H or C atoms of the cyclohexyl groups are larger than in complexes with notable agostic interactions.[12e,f,15] An agostic interaction can also be excluded in solution, as proven by low-temperature NMR spectroscopy in solution. We performed DFT calculations on the series of model compounds *trans*-$[Pt\{B(Br)(R)\}Br(PCy_3)_2]$ (R = NMe_2, **neut**; R = Fc, **neut_Fc**), *trans*-$[Pt\{B(Br)(R)\}(PCy_3)_2]^+$ (R = NMe_2, **cat1**; R = Fc, **cat1_Fc**), *trans*-$[Pt\{=B(R)(4\text{-}Pic)\}Br(PCy_3)_2]^+$ (R = NMe_2, **cat2**; R = Fc, **cat2_Fc**), and *trans*-$[Pt\{=B(R)(4\text{-}Pic)\}(PCy_3)_2]^{2+}$ (R = NMe_2, **dicat**; R = Fc, **dicat_Fc**) in the presence of $[BPh_4]^-$ as a simplified model counteranion (Figure 2). As both substituted systems present the same trend in their electronic structure, we will only refer to the dimethylamino-substituted complexes in the following discussion (that is, R = NMe_2; see the Supporting Information for the results regarding the Fc-substituted complexes). A typical structure of **dicat** displays bonding distances and angles similar to those of crystallographically observed molecular structure of **2a** (Pt–B 200.7, Pt–P1 235.3, Pt–P1 235.8, B–N1 138.4, B–N2 154.4 pm; P1-Pt-P2 164.15, P1-Pt-B 98.70, P2-Pt-B 97.06°). The shortest Pt–C separation of 328.64 pm in the model complex **dicat** is even longer than the crystallographically observed value, indicating the absence of any agostic interaction. This observation is also supported by the NBO analysis, which gives positive charges for both P atoms (+1.100 and +1.112 e^-) and a total charge of roughly +0.471 for each phosphine ligand (+0.461 and +0.481 e^-), whereas the platinum atom is almost neutral (0.153 e^-). The picoline fragment carries a positive charge of +0.353 e^-, which

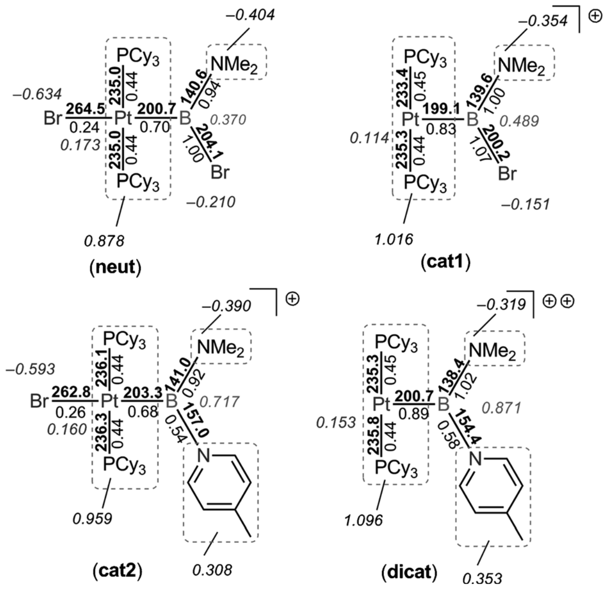

Figure 2. Results of the NBO analysis on the optimized structures of the complexes **neut**, **cat1**, **cat2**, and **dicat**. For the metrics, bond distances [pm] are shown in bold, bond orders in normal font, and natural charges [e^-] of atoms and fragments are presented in italics. (Platinum is included in the defined fragment.)

compensates the negative charge of the amino substituent ($-0.319\ e^-$). The analysis of the electrostatic potential of all participating precursors in the synthesis of **dicat** indicates an increase of the σ-donor ability of the boron-based ligand, and therefore its *trans* influence, by exchanging the σ-withdrawing bromine substituent at the boron atom with the σ-donating 4-picoline group. This result clearly indicates the similarities of boryl and base-stabilized borylene ligands.

We also investigated the electronic structure in these complexes by means of NBO calculations. According to the energy estimation from second-order perturbation theory, we found that throughout this series, there is a stabilizing interaction of electron donation from the Pt–P σ-bond of one of the phosphines to the Pt–B π*-bond on the order of 42–43 kcal mol^{-1}, and a similar interaction from the Pt–B π-bond to the Pt–P σ*-bond that varies more notably: 49.4, 49.0, 44.5, and 46.0 kcal mol^{-1} from **neut** to **dicat**, respectively. We found a favorable interaction between the σ and π natural bond orbitals of Pt–B that can account for the donation/back-donation existing in these systems (Table 1).

Table 1: Natural molecular orbital analysis of the Pt–B bond for the series of model complexes of **1**–**4**.

	Occupied two-center Pt–B bond	Unoccupied two-center Pt-B antibond	E[a] [kcal mol^{-1}]
neut	$0.70(sd^{1.3})_{Pt}+0.71(sp^{1.3})_B$	$0.71(sd^{1.3})_{Pt}-0.70(sp^{1.3})_B$	7.5
cat1	$0.75(sd^{1.3})_{Pt}+0.66(sp^{1.6})_B$	$0.66(sd^{1.3})_{Pt}-0.75(sp^{1.6})_B$	15.9
cat2	$0.69(sd^{1.2})_{Pt}+0.73(sp^{1.0})_B$	$0.73(sd^{1.2})_{Pt}-0.69(sp^{1.0})_B$	6.0
dicat	$0.74(sd^{1.3})_{Pt}+0.67(sp^{1.3})_B$	$0.67(sd^{1.3})_{Pt}-0.74(sp^{1.3})_B$	16.3

[a] Energies were obtained from the second-order perturbation theory analysis.

Looking at the coefficients of the NBOs in Table 1, we can establish the direction of the donation (and thus, back-donation) between the metal center and the boryl ligand. In the neutral species **neut**, as the bromine atom is *trans* to the boron, we can expect that the net donation is in the direction Pt←B, in agreement with the NBO coefficients of the two-center Pt–B bond. In **cat1**, the influence of the boron-bound bromine atom reverses the net direction of the donation to Pt→B in **cat1**. The donation ratio in **cat2**, in which the halogen is bound to the Pt atom and 4-picoline is bound to the boron atom, is Pt←B. The electron deficiency at the boron atom in **dicat**, which is partially ameliorated by the 4-picoline donor, results in an overall electron donation from Pt→B. The stabilization energies presented in Table 1 are also in line with this reasoning as the larger imbalances occur when halides are removed and boron requires more electron donation from the metal center.

The stepwise synthesis of *trans*-$[Pt\{=B(Fc)(4\text{-}Pic)\}(PCy_3)_2]^{2+}$ (**2b**) from *trans*-$[Pt\{B(Br)(Fc)\}Br(PCy_3)_2]$ (**6**) is accompanied by significant color changes in every reaction step. To shed some light on the optophysical properties of the Fc-substituted system **2b**, we recorded UV/Vis spectra of all of the isolated intermediates. The red-orange color of a dichloromethane solution of the neutral boryl complex *trans*-$[Pt\{B(Br)(Fc)\}Br(PCy_3)_2]$ ($\lambda_{max1}=358$ nm, $\varepsilon_1=1211$ L mol^{-1} cm^{-1}, $\lambda_{max2}=483$ nm, $\varepsilon_2=700$ L mol^{-1} cm^{-1}) intensifies when the halogen ligand is abstracted and the T-shaped, cationic boryl complex **5** is formed ($\lambda_{max1}=360$ nm, $\varepsilon_1=2993$ L mol^{-1} cm^{-1}, $\lambda_{max2}=484$ nm, $\varepsilon_2=1200$ L mol^{-1} cm^{-1}). The complexes with the base-stabilized borylene ligands (**1b**, $\lambda_{shoulder}=420$ nm, $\varepsilon_{shoulder}=545$ L mol^{-1} cm^{-1}, $\lambda_{max1}=558$ nm, $\varepsilon_1=1070$ L mol^{-1} cm^{-1}; **2b**, $\lambda_{shoulder}=495$ nm, $\varepsilon_{shoulder}=960$ L mol^{-1} cm^{-1}, $\lambda_{max1}=589$ nm, $\varepsilon_1=1176$ L mol^{-1} cm^{-1}) show strong bathochromically shifted absorption maxima relative to those of the Fc-substituted boryl complexes **5** and **6**, of which the dicationic representative shows maxima close to those of $[Fc][PF_6]$. This finding, along with the deep purple color of **1b** and the dark blue color of **2b**, suggests the partial oxidation of the ferrocenyl group with increased total charge of the complex fragment. Quantum-chemical electrostatic potential analysis of *trans*-$[Pt\{=B(Fc)(4\text{-}Pic)\}(PCy_3)_2]^{2+}$ (**dicat_Fc**) supports this suggestion, as an electron depletion at the ferrocenyl group was found (see the Supporting Information).

Owing to the higher stability of **2a**, which can be ascribed to the π-conjugation of the amino group to the boron atom, we performed reactivity studies on this compound rather than the ferrocenyl compound **2b**. Freezing a yellow solution of **2a** in CD_2Cl_2 in a Young NMR tube, evacuation and purging with N_2, N_2O, or CO_2 followed by thawing and mixing does not lead to any reaction. However, the same procedure with CO results in a colorless solution. The $^{31}P\{^1H\}$ NMR spectrum indicates the formation of a new, symmetrical platinum phosphine complex (**4a**) with a chemical shift of $\delta=29.6$ ppm ($^1J_{P\text{-}Pt}=2137$ Hz), presumably the product of CO addition *trans* to the boryl moiety. A band at 2094 cm^{-1} in the infrared spectrum of **4a** indicates the presence of a classically bound carbonyl ligand. Addition of acetonitrile to a yellow solution of **2a** in CD_2Cl_2 also leads to a colorless solution. In this case, a new signal in the ^{31}P NMR spectrum was found at $\delta=30.1$ ppm ($^1J_{P\text{-}Pt}=2483$ Hz), also suggesting the formation of a symmetrical product (**3a**) with coordination of the base at the previously vacant coordination site at the platinum center.

Highly positively charged metal complexes are generally coordinatively and/or electronically saturated—this helps to offset the electrophilicity caused by the charge. By halide abstraction from cationic base-stabilized borylene complexes, we have prepared two examples of dicationic, three-coordinate platinum complexes. The complexes prepared herein are the first dicationic complexes of Group 10 metals with a coordination number lower than four and a formal VE count lower than 16. Remarkably, despite their extreme electronic and coordinative unsaturation, no agostic interactions were observed, and the complexes underwent associative ligation only with small Lewis donors, such as CO and acetonitrile. DFT calculations suggest that the charge at the platinum center changes little as the complex changes from neutral to cationic to dicationic, and that this effect may be due to some spreading of the positive charges onto the boron atom and pyridine base. In the case of the Fc-substituted complexes **1b** and **2b**, their color and UV/Vis spectra suggest that there is significant electron transfer from the ferrocenyl group to the Pt–B core, leading to some amount of oxidation of the iron and thus some Fe^{III} character.

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[1] a) G. Alibrandi, L. M. Scolaro, R. Romeo, *Inorg. Chem.* **1991**, *30*, 4007–4013; b) U. Christmann, R. Vilar, *Angew. Chem.* **2005**, *117*, 370–378; *Angew. Chem. Int. Ed.* **2005**, *44*, 366–374; c) R. J. Puddephatt, *Angew. Chem.* **2002**, *114*, 271–273; *Angew. Chem. Int. Ed.* **2002**, *41*, 261–263.

[2] V. Lavallo, Y. Canac, A. DeHope, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 7402–7405; *Angew. Chem. Int. Ed.* **2005**, *44*, 7236–7239.

[3] a) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560–564; b) G. Gerdes, P. Chen, *Organometallics* **2004**, *23*, 3031–3036; c) T. G. Driver, M. W. Day, J. A. Labinger, J. E. Bercaw, *Organometallics* **2005**, *24*, 3644–3654; d) A. F. Heyduk, T. G. Driver, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2004**, *126*, 15034–15035.

[4] a) K. Aikawa, Y. Hioki, K. Mikami, *J. Am. Chem. Soc.* **2009**, *131*, 13922–13923; b) K. Aikawa, K. Honda, S. Mimura, K. Mikami, *Tetrahedron Lett.* **2011**, *52*, 6682–6686.

[5] a) C. Hahn, P. Morvillo, E. Herdtweck, A. Vitagliano, *Organometallics* **2002**, *21*, 1807–1818; b) K. Siegmann, P. S. Pregosin, L. M. Venanzi, *Organometallics* **1989**, *8*, 2659–2664; c) C. Hahn, M. E. Cucciolito, A. Vitagliano, *J. Am. Chem. Soc.* **2002**, *124*, 9038–9039; d) T. G. Driver, T. J. Williams, J. A. Labinger, J. E. Bercaw, *Organometallics* **2007**, *26*, 294–301; e) R. Bertani, R. A. Michelin, M. Mozzon, A. Sassi, M. Basato, A. Biffis, G. Martinati, M. Zecca, *Inorg. Chem. Commun.* **2001**, *4*, 281–284.

[6] a) J. H. Koh, M. R. Gagne, *Angew. Chem.* **2004**, *116*, 3541–3543; *Angew. Chem. Int. Ed.* **2004**, *43*, 3459–3461; b) J. G. Sokol, C. S. Korapala, P. S. White, J. J. Becker, M. R. Gagné, *Angew. Chem.* **2011**, *123*, 5776–5779; *Angew. Chem. Int. Ed.* **2011**, *50*, 5658–5661.

[7] J. Carreras, M. Patil, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2012**, *134*, 16753–16758.

[8] a) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685–2722; b) H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924–3957.

[9] a) H. Braunschweig, K. Radacki, D. Rais, D. Scheschkewitz, *Angew. Chem.* **2005**, *117*, 5796–5799; *Angew. Chem. Int. Ed.* **2005**, *44*, 5651–5654; b) H. Braunschweig, K. Radacki, K. Uttinger, *Chem. Eur. J.* **2008**, *14*, 7858–7866.

[10] H. Braunschweig, K. Radacki, K. Uttinger, *Organometallics* **2008**, *27*, 6005–6012.

[11] a) U. Fekl, K. I. Goldberg, *Adv. Inorg. Chem.* **2003**, *54*, 259–320; b) H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378–1399; c) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203; d) M. D. Butts, B. L. Scott, G. J. Kubas, *J. Am. Chem. Soc.* **1996**, *118*, 11831–11843.

[12] a) N. Carr, L. Mole, A. G. Orpen, J. L. Spencer, *J. Chem. Soc. Dalton Trans.* **1992**, 2653–2662; b) N. Carr, B. J. Dunne, A. G. Orpen, J. L. Spencer, *J. Chem. Soc. Chem. Commun.* **1988**, 926–928; c) J. L. Spencer, G. S. Mhinzi, *J. Chem. Soc. Dalton Trans.* **1995**, 3819–3824; d) L. Mole, J. L. Spencer, N. Carr, A. G. Orpen, *Organometallics* **1991**, *10*, 49–52; e) M. J. Ingleson, M. F. Mahon, A. S. Weller, *Chem. Commun.* **2004**, 2398–2399; f) W. Baratta, S. Stoccoro, A. Doppiu, E. Herdtweck, A. Zucca, P. Rigo, *Angew. Chem.* **2003**, *115*, 109–113; *Angew. Chem. Int. Ed.* **2003**, *42*, 105–109; g) L. H. Shultz, M. Brookhart, *Organometallics* **2001**, *20*, 3975–3982; h) F. M. Conroy-Lewis, L. Mole, A. D. Redhouse, S. A. Litster, J. L. Spencer, *J. Chem. Soc. Chem. Commun.* **1991**, 1601–1603.

[13] W. H. Lam, K. C. Lam, Z. Lin, S. Shimada, R. N. Perutz, T. B. Marder, *Dalton Trans.* **2004**, 1556–1562.

[14] M. Hasegawa, Y. Segawa, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2012**, *51*, 6956–6960.

[15] A. Toupadakis, G. J. Kubas, W. A. King, B. L. Scott, J. Huhmann-Vincent, *Organometallics* **1998**, *17*, 5315–5323.