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## Synthesis and Reactivity of Tungsten Vinylallene Complexes

Ding-Jen Chen, Pei-Chen Ting, Ying-Chih Lin,\* Gene-Hsiang Lee and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

Protonation at one of the phenylacetylide substituents of the allylic complexes  $[W(cp)(CO)_2\{\eta^3-H_2CC[C(C\equiv CPh)_2]CH_2R\}]$  ( $cp = \eta^5-C_5H_5$ ), including the first cationic tungsten–ruthenium allylic vinylidene complex,  $R = C(Ph)=C=Ru(cp)(PPh_3)_2$  (crystal structure), gave  $\eta^4$ -vinylallene complexes.

The preparation of transition-metal allylic complexes and trimethylenemethane complexes<sup>1</sup> as well as their synthetic applications<sup>2</sup> have attracted a great deal of attention recently. However, few examples of transition-metal complexes containing co-ordinated conjugated vinylallene<sup>3</sup> have been reported and their synthetic relationship to the above complexes has been mostly unnoticed. In this communication we report the synthesis of a number of vinylallene complexes from the reactions of  $[W(cp)(CO)_2\{\eta^3-H_2CC[C(C\equiv CPh)_2]CH_2\}]^+ \mathbf{1}$  ( $cp = \eta^5-C_5H_5$ ) with various nucleophiles followed by protonation. The nucleophilic addition occurs at the non-substituted terminal carbon of the alkyne ligand and subsequent protonation at the acetylide group. Thus from the reaction of  $\mathbf{1}$  with  $[Ru(cp)(PPh_3)_2(C\equiv CPh)]$  under mild conditions, the first tungsten–ruthenium dinuclear cationic complex  $[W(cp)(CO)_2\{\eta^3-H_2CC[C(C\equiv CPh)_2]CH_2C(Ph)=C=Ru(cp)(PPh_3)_2\}]^+ \mathbf{2a}$  is isolated. Subsequent protonation yields a dinuclear dicationic complex with a  $\mu$ - $\eta^4, \eta^1$ -vinylallene–vinylidene bridging ligand.

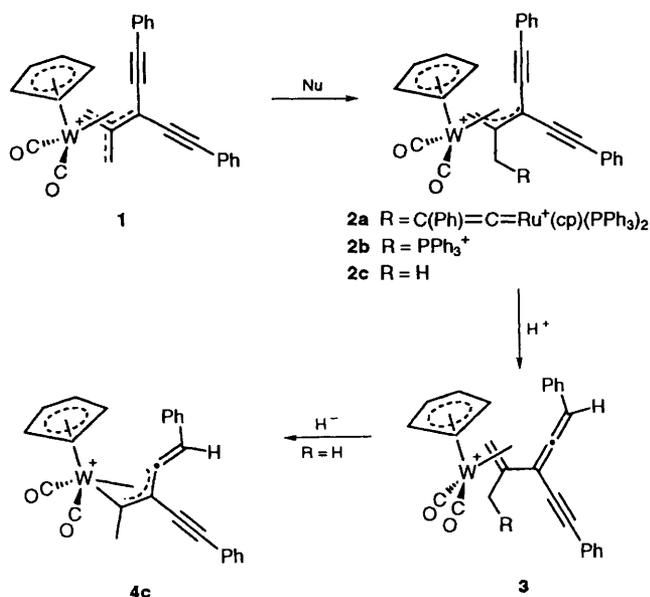
Complex  $\mathbf{1}$  was prepared from the reaction of  $[W(cp)(CO)_2\{\eta^3-H_2CC[C(OH)(C\equiv CPh)_2]CH_2\}]$  with  $HBF_4$  in 89% yield and its reactions with  $[Ru(cp)(PPh_3)_2(C\equiv CPh)]$ ,  $PPh_3$  or  $H^-$  cleanly produce the allylic complexes  $[W(cp)(CO)_2\{\eta^3-H_2CC[C(C\equiv CPh)_2]CH_2R\}]$  [ $R = (Ph_3P)_2(cp)Ru=C=CPh^+ \mathbf{2a}$ ,  $PPh_3^+ \mathbf{2b}$  or  $H \mathbf{2c}$ ] at 0 °C in MeCN. All nucleophilic additions occur exclusively at the non-substituted terminus of the trimethylenemethane ligand. In the reaction of  $\mathbf{1}$  with  $[Ru(cp)(PPh_3)_2(C\equiv CPh)]$  the triple bond of the latter serves as a nucleophilic centre and thus the deep red tungsten–ruthenium dinuclear complex  $\mathbf{2a}$  is produced, see Scheme 1. In the reaction of  $\mathbf{1}$  with  $PPh_3$  the phosphine attacks the same position giving  $\mathbf{2b}$  and  $\mathbf{2c}$  is prepared from hydride addition. The spectroscopic data† for  $\mathbf{2}$  are consistent with their formulations. In the IR spectra of  $\mathbf{2a}$  and  $\mathbf{2b}$  the  $\nu_{CO}$  absorptions (all less than 2000  $cm^{-1}$ ) indicate a neutral  $(cp)W(CO)_2$  moiety inferring localization of the cationic charge at the Ru atom and  $PPh_3$ , respectively. In the  $^1H$  NMR spectra the *syn* and *anti* protons of  $\mathbf{2}$  appear as two broad resonances in the normal allylic region of  $\delta$  3.15–2.70. For  $\mathbf{2a}$  and  $\mathbf{2b}$  the other methylene protons appear as multiplet resonances at lower field ( $\delta$  4.61–3.23). In the  $^{31}P$  NMR spectrum of  $\mathbf{2a}$  the resonances of the two  $PPh_3$  ligands appear as doublets at  $\delta$  41.8 and 43.1 with  $J_{PP} = 27.0$  Hz, in contrast to a singlet resonance for similar ruthenium complexes<sup>4</sup> which show fluxionality of the vinylidene ligand. The inequivalence of the two  $PPh_3$  in  $\mathbf{2a}$  is attributed to the steric bulk of the tungsten–allyl moiety hindering rotation of the vinylidene ligand.

The structure of complex  $\mathbf{2a}$  was confirmed by a single-crystal X-ray diffraction analysis‡ and an ORTEP<sup>5</sup> drawing is shown in Fig. 1. The Ru–C(24) [1.86(1) Å], C(24)–C(23) [1.31(2) Å] and Ru–C(24)–C(23) [170(1)°] are typical for

cationic ruthenium vinylidene complexes. The  $\alpha, \alpha, \beta$ -tri-substituted allylic group adopts an *endo* conformation with W–C (centre) 2.28(1) Å being the shortest among the three W–C

† Proton (300 MHz) and  $^{13}C$ - $\{^1H\}$  (75 MHz) (298 K,  $CD_3CN$ , relative to  $SiMe_4$ ,  $J$  in Hz),  $^{31}P$  (121.5 MHz) NMR ( $H_3PO_4$  external standard). Complex  $\mathbf{1}$ : IR (MeCN)  $\nu_{CO}$  2069s, 2022s  $cm^{-1}$ ;  $^1H$  NMR,  $\delta$  7.53–7.38 (m, 10 H, Ph), 5.83 (s, 5 H, cp), 3.77 (s, 2 H, *syn*-CH<sub>2</sub>), 3.51 (s, 2 H, *anti*-CH<sub>2</sub>);  $^{13}C$  NMR,  $\delta$  201.2 (CO), 132.7–129.7 (Ph), 122.1 (CCH<sub>2</sub>), 93.9 (cp), 90.3 ( $\equiv C$ ), 86.5 ( $\equiv C$ ), 68.5 (CC $\equiv$ CPh), 54.5 (CH<sub>2</sub>); mass spectrum (FAB),  $m/z$  559 ( $M^+ - BF_4$ ), 503 ( $M^+ - 2CO - BF_4$ ),  $\mathbf{2a}$  (Found: C, 55.91; H, 3.54. Calc. for  $C_{76}H_{59}BF_4O_2P_2RuW \cdot CH_2Cl_2$ : C, 56.35; H, 3.35%) IR (MeCN)  $\nu_{CO}$  1953s, 1884s  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ ),  $\delta$  7.37–6.78 (m, 45 H, Ph), 5.34 (s, 5 H, cp), 5.10 (s, 5 H, cp), 3.77 (d,  $^2J_{HH} = 14.1$ , 1 H, CH), 3.23 (d,  $^2J_{HH} = 14.1$ , 1 H, CH), 2.90 (s, 1 H, *syn*-CH), 2.70 (s, 1 H, *anti*-CH);  $^{13}C$  NMR ( $CDCl_3$ ),  $\delta$  134.5–123.5 (Ph), 93.9 (cp), 92.9 (cp), 35.5 (CH<sub>2</sub>CPh $\equiv$ ), 29.7 (CC $\equiv$ CPh), 27.1 (CH<sub>2</sub>);  $^{31}P$  NMR ( $CDCl_3$ ),  $\delta$  43.1 (d,  $^2J_{PP} = 27$ ), 41.8 (d,  $^2J_{PP} = 27$ ); mass spectrum (FAB),  $m/z$  1438 ( $M^+$ ), 1351 ( $M^+ - BF_4$ ), 1033 ( $M^+ - BF_4 - PPh_3 - 2 CO$ ), 771 ( $M^+ - BF_4 - 2PPh_3 - 2 CO$ ).  $\mathbf{2b}$ : IR (tetrahydrofuran, thf)  $\nu_{CO}$  1955s, 1884s  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ ),  $\delta$  7.80–7.23 (m, 25 H, Ph), 5.40 (s, 5 H, cp), 4.61 (dd, 1 H, CH), 4.18 (dd, 1 H, CH), 2.95 (s, 1 H, *syn*-CH), 2.78 (s, 1 H, *anti*-CH);  $^{13}C$  NMR ( $CDCl_3$ ),  $\delta$  224.0, 220.9 (CO), 137.1–115.6 (Ph), 94.7 (CCH<sub>2</sub>P), 93.3 (cp), 90.7 ( $\equiv C$ ), 87.7 ( $\equiv C$ ), 85.9 ( $\equiv C$ ), 82.8 ( $\equiv C$ ), 36.2 (CH<sub>2</sub>P), 29.5 (CC $\equiv$ CPh), 27.5 (CH<sub>2</sub>CCH<sub>2</sub>P);  $^{31}P$  NMR ( $CDCl_3$ ),  $\delta$  26.7 (s); mass spectrum (FAB),  $m/z$  821 ( $M^+ - BF_4$ ), 765 ( $M^+ - BF_4 - 2 CO$ ), 559 ( $M^+ - BF_4 - PPh_3$ ).  $\mathbf{2c}$ : IR (MeCN)  $\nu_{CO}$  1952s, 1879s  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ ),  $\delta$  7.50–7.24 (m, 10 H, Ph), 5.40 (s, 5 H, cp), 3.15 (br, 1 H, *syn*-CH), 2.97 (s, 1 H, *anti*-CH), 2.75 (s, 3 H, CH<sub>3</sub>);  $^{13}C$  NMR ( $CDCl_3$ ),  $\delta$  228.8, 224.4 (CO), 131.8–123.6 (Ph), 101.7 (CH<sub>2</sub>CCH<sub>3</sub>), 94.5 ( $\equiv C$ ), 92.9 (cp), 92.2 ( $\equiv C$ ), 84.4 ( $\equiv C$ ), 80.5 ( $\equiv C$ ), 29.2 (CC $\equiv$ CPh), 28.5 (CH<sub>2</sub>CCH<sub>3</sub>), 22.9 (CH<sub>3</sub>); mass spectrum (FAB),  $m/z$  560 ( $M^+$ ), 504 ( $M^+ - 2 CO$ ).  $\mathbf{3a}$ : IR (KBr)  $\nu_{CO}$  2073s, 2024s  $cm^{-1}$ ;  $^1H$  NMR,  $\delta$  7.68–6.87 (m, 45 H, Ph), 5.68 (s, 5 H, cp), 5.31 (s, 5 H, cp), 4.23 (d,  $^2J_{HH} = 14$ , 1 H, CH<sub>2</sub>C $\equiv$ ), 3.40 (d,  $^2J_{HH} = 14$ , 1 H, CH<sub>2</sub>C $\equiv$ ), 2.48 (br, 1 H, =CH<sub>2</sub>), 1.81 (br, 1 H, =CH<sub>2</sub>);  $^{31}P$  NMR,  $\delta$  43.5 (d,  $^2J_{PP} = 26.6$ ), 41.6 (d,  $^2J_{PP} = 26.6$ ); mass spectrum (FAB),  $m/z$  1439 ( $M^+ - BF_4$ ), 1352 ( $M^+ - 2BF_4$ ), 1324 ( $M^+ - 2BF_4 - CO$ ), 1034 ( $M^+ - 2BF_4 - 2 CO - PPh_3$ ).  $\mathbf{3b}$ : IR (KBr)  $\nu_{CO}$  2068s, 2022s  $cm^{-1}$ ;  $^1H$  NMR,  $\delta$  7.97–7.28 (m, 25 H, Ph), 6.06 (s, 5 H, cp), 5.02 (t,  $^2J_{HH} = 2J_{HP} = 4$ , 1 H, CH<sub>2</sub>P), 4.58 (t,  $^2J_{HH} = 2J_{HP} = 4$ , 1 H, CH<sub>2</sub>P), 2.37 (br, 1 H, =CH<sub>2</sub>), 1.65 (br, 1 H, =CH<sub>2</sub>);  $^{31}P$  NMR,  $\delta$  27.7 (s); mass spectrum (FAB),  $m/z$  909 ( $M^+ - BF_4$ ), 822 ( $M^+ - 2BF_4$ ), 766 ( $M^+ - 2BF_4 - 2 CO$ ), 504 ( $M^+ - 2BF_4 - 2 CO - PPh_3$ ).  $\mathbf{3c}$ : IR (KBr)  $\nu_{CO}$  2067s, 2013s  $cm^{-1}$ ;  $^1H$  NMR,  $\delta$  8.01–7.38 (m, 10 H, Ph), 5.88 (s, 5 H, cp), 2.86 (s, 3 H, CH<sub>3</sub>), 2.72 (br, 1 H, =CH<sub>2</sub>), 1.86 (br, 1 H, =CH<sub>2</sub>); mass spectrum (FAB),  $m/z$  561 ( $M^+ - BF_4$ ), 505 ( $M^+ - BF_4 - 2 CO$ ).  $\mathbf{4c}$  (Found: C, 57.44; H, 4.01. Calc. for  $C_{26}H_{19}O_2W$ : C, 57.57; H, 4.12%) IR (MeCN)  $\nu_{CO}$  1942s, 1868s  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ ),  $\delta$  7.95 (s, 1 H, =CHPh), 7.61–7.20 (m, 10 H, Ph), 5.51 (s, 5 H, cp), 2.18 (s, 3 H, CH<sub>3</sub>), 1.67 (s, 3 H, CH<sub>3</sub>);  $^{13}C$  NMR ( $CDCl_3$ ),  $\delta$  229.8, 215.9 (CO), 154.3 (C=CHPh), 138.8–122.8 (Ph), 128.7 (C=CHPh), 94.4 (cp), 91.6 (CC $\equiv$ CPh), 85.0 (C $\equiv$ CPh), 80.9 (C $\equiv$ CPh), 49.0 (CCH<sub>3</sub>), 28.1 (CH<sub>3</sub>), 27.3 (CH<sub>3</sub>); mass spectrum (FAB),  $m/z$  562 ( $M^+$ ), 534 ( $M^+ - CO$ ), 506 ( $M^+ - 2 CO$ ).

‡ Crystal data:  $C_{76}H_{59}BF_4O_2P_2RuW \cdot 3CH_2Cl_2$ ,  $M = 1692.76$ , triclinic, space group,  $PT$ ,  $a = 13.171(4)$ ,  $b = 14.797(6)$ ,  $c = 19.960(6)$  Å,  $\alpha = 92.02(3)$ ,  $\beta = 100.17(3)$ ,  $\gamma = 100.39(3)^\circ$ ,  $U = 3757.1(22)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.496$  g  $cm^{-3}$ , crystal dimensions  $0.15 \times 0.40 \times 0.40$  mm,  $\mu = 19.107$   $cm^{-1}$ , observed reflections 5618 [ $I > 2\sigma(I)$ ], total 9799,  $2\theta_{max} = 45.0^\circ$ . An absorption correction was carried out (transmission range 0.858–1.000). The structure was solved by Patterson synthesis then refined by standard least-squares and Fourier-difference techniques;  $w = 1/\sigma^2(F_o)$ . Non-hydrogen atoms were refined by using anisotropic thermal parameters. Three  $CH_2Cl_2$  molecules per complex molecule were also observed. Total number of parameters: 793.  $R = 0.066$ ,  $R' = 0.069$ ; goodness of fit = 2.64,  $\Delta\rho = -1.36$  to  $1.37$  e Å<sup>-3</sup>. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 Nu = Ru(cp)(PPh<sub>3</sub>)<sub>2</sub>(C≡CPh) **2a**, PPh<sub>3</sub> **2b** or NaBH<sub>4</sub> **2c**

(allyl) bonds. The newly formed C(22)–C(23) bond of 1.50(2) Å is a normal single bond.

In the protonation reaction of complex **2** the C≡CPh group of the allylic ligand serves as a proton acceptor, thus the η<sup>4</sup>-vinylallene product **3** is produced cleanly. For example, protonation of **2a** by HBF<sub>4</sub> gives **3a** in quantitative NMR yield, see Scheme 1. Protonation of **2b** and **2c** also gives **3b** and **3c**, respectively. In the IR spectrum of **3a** the ν<sub>CO</sub> absorptions, all at >2000 cm<sup>-1</sup>, indicate the cationic character of the tungsten centre. In the <sup>1</sup>H NMR spectrum of **3a** the two broad resonances at δ 2.48 and 1.81 are assigned to the two *gem*-vinylic protons. The relatively upfield shift is due to co-ordination of the vinyl group. The two doublets, at δ 4.23 and 3.40 are assigned to the other methylene group. The resonances of the terminal allenyl proton and the aromatic protons are overlapped. The configuration of the phenyl group at the allene terminal is not clear at this time, however judging by the fact that protonation should occur at the most electron-rich site one could reasonably anticipate a *syn* configuration (with respect to W). Namely direct protonation at the acetylide group should be more favourable than protonation at the metal followed by proton transfer. An η<sup>4</sup>-vinylallene ligand in an iron complex was reported recently.<sup>6</sup> Two methods are known for the preparation of such complexes: treatment of a vinylketene complex with a stabilized Wittig reagent<sup>7</sup> and simple complexation of vinylallene to a metal.<sup>6</sup> Our method provides another approach for such a compound.

The reaction of an excess Na[BH<sub>3</sub>(CN)] with complex **3c** gave neutral **4c** in high yield. Namely, addition of hydride occurs at the terminal CH<sub>2</sub> yielding **4c** with two Me groups, *i.e.* the η<sup>4</sup>-vinylallene is converted into an η<sup>3</sup>-vinylallylic ligand. In the <sup>1</sup>H NMR spectrum the two singlets at δ 2.18 and 1.67 are assigned to the two methyl groups and the singlet at δ 7.95 with relative integration of 1 H is assigned to the vinylic proton; the assignment was confirmed by a deuteration study. The ν<sub>CO</sub> at 1942 and 1868 cm<sup>-1</sup> indicates the neutral character of the metal centre. Vinyl substituents at allylic terminals are known in a few previous examples.<sup>8</sup> The configuration of the phenyl relative to the allylic group is not known. Similar reactions of **3a** and **3b** give complex mixtures. Owing to the dicationic charges of **3a** and **3b** the addition of hydride might occur at two possible sites. No attempt was made to isolate the product.

We have previously reported the synthesis of the analogous 1,1-dimethyltrimethylenemethane complex<sup>9</sup> [W(cp)(CO)<sub>2</sub>{η<sup>4</sup>-H<sub>2</sub>CC(CMe<sub>2</sub>)CH<sub>2</sub>}]<sup>+</sup> **5**, which shows different reactivity from

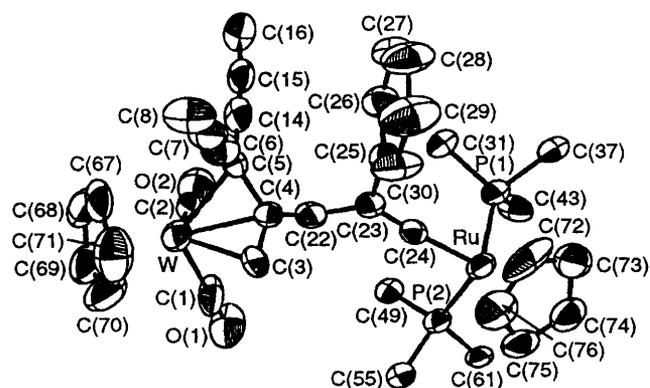


Fig. 1 Structure of the cation of complex **2a** showing the atom numbering scheme and with 50% probability ellipsoids; all the phenyl groups of the phosphine and of the allylic ligand are omitted for clarity. Atoms C(8), C(16), C(31), C(37), C(43), C(49), C(55) and C(61) are the *ipso* phenyl carbons. Only the phenyl group of the vinylidene ligand is shown

that of **1**. Depending on the nucleophiles used, additions could occur either at the substituted or at the non-substituted site of trimethylenemethane ligand of **5**. For example, the addition of H<sup>-</sup> and N<sub>3</sub><sup>-</sup> occurs at the substituted site producing [W(cp)(CO)<sub>2</sub>{η<sup>3</sup>-H<sub>2</sub>CC(CHMe<sub>2</sub>)CH<sub>2</sub>}] and [W(cp)(CO)<sub>2</sub>{η<sup>3</sup>-H<sub>2</sub>CC[C(N<sub>3</sub>)Me<sub>2</sub>]CH<sub>2</sub>}] respectively. On the other hand, addition of thio nucleophiles occurs at the non-substituted site of **5**, similar to that of **2**. Interestingly, in the reaction of **5** with [Ru(cp)(PPh<sub>3</sub>)<sub>2</sub>(C≡CPh)] the acidic proton of the methyl groups in **5** prohibits formation of the addition product, but the deprotonation reaction produces [W(cp)(CO)<sub>2</sub>{η<sup>3</sup>-H<sub>2</sub>CC-[C(Me)=CH<sub>2</sub>]CH<sub>2</sub>}] and the vinylidene complex [Ru(cp)(PPh<sub>3</sub>)<sub>2</sub>(=C=CHPh)]<sup>+</sup>.

In summary, in the reaction of the cationic 1,1-di(phenyl-ethynyl)trimethylenemethane complex with nucleophiles, the electron-rich acetylide group controls the site of nucleophilic addition. Furthermore, subsequent protonation at this group also provides an entry to a rare class of vinylallene complex. The synthesis and reactivity of these complexes are currently under investigation.

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#### References

- M. Rosenblum, *J. Organomet. Chem.*, 1986, **300**, 191; A. Wojcicki, *Coord. Chem. Rev.*, 1990, **105**, 35; D. M. T. Chan, in *Comprehensive Organic Syntheses*, ed. B. M. Trost, Pergamon, New York, 1991, vol. 5, pp. 271–314; M. E. Welker, *Chem. Rev.*, 1992, **92**, 97.
- B. M. Trost and D. M. T. Chan, *J. Am. Chem. Soc.*, 1983, **105**, 2326; L. S. Hegeudus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, CA, 1994, pp. 261–305.
- L. S. Trifonov, A. S. Orahovats, R. Prewo and H. Heimgartner, *Helv. Chim. Acta*, 1988, **71**, 551; S. P. Saberi and S. E. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1992, 259.
- M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197.
- C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- C. E. Kerr, B. E. Eaton and J. A. Kaduk, *Organometallics*, 1995, **14**, 269.
- L. Hill, S. P. Saberi, A. M. Z. Slawin, S. E. Thomas and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 1290.
- H. L. Stokes, T. L. Smalley, jun., M. L. Hunter, M. E. Welker and A. L. Rheingold, *Inorg. Chim. Acta*, 1994, **220**, 305.
- I.-Y. Wu, M.-C. Chen, Y. C. Lin and Y. Wang, *Organometallics*, 1993, **12**, 1686.

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