

# Synthesis and characterization of a bimetallic iridium complex with a ten $sp^2$ -carbon chain bridge†‡

Lei Gong, Liqiong Wu, Yumei Lin, Hong Zhang, Fangzu Yang, Tingbin Wen and Haiping Xia\*

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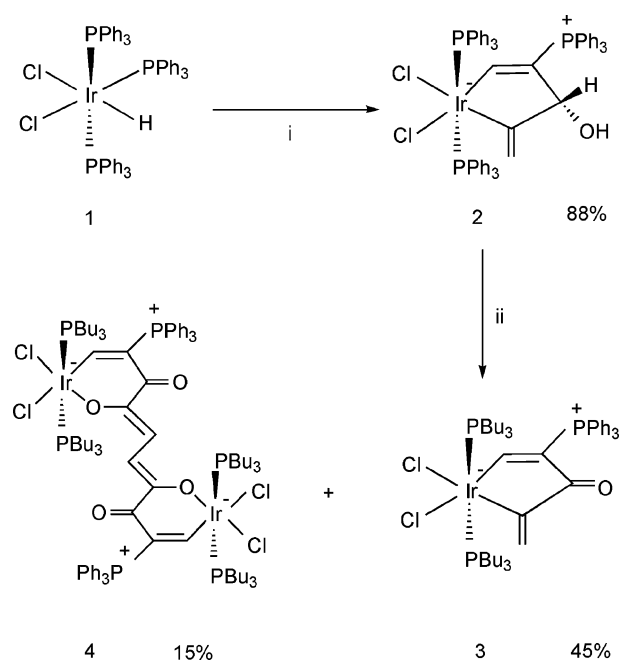
A special  $sp^2$ -carbon chain bridged bimetallic iridium complex has been synthesized and characterized; the compound has excellent air-stability, thermo-stability and electrochemical properties.

Organic compounds having conjugated  $\pi$ -systems can act as electronic bridges between transition metal atoms. Numerous experimental and theoretical studies on dinuclear organometallic compounds with two metal centres linked by a conjugated organic bridge have been reported,<sup>1–8</sup> especially those of ruthenium,<sup>1</sup> iron,<sup>2</sup> rhodium,<sup>3</sup> and platinum.<sup>4</sup> In contrast, conjugated bimetallic iridium complexes<sup>5</sup> are rare up to now. Additionally, many conjugated dinuclear complexes with  $sp$ -carbon bridges:  $-C_x-$ <sup>6</sup> or mixed bridges such as  $-(C\equiv C)_x-(C_6H_4)_y-(C\equiv C)_x-$  are known,<sup>7</sup> while those with pure  $sp^2$ -carbon bridges, such as  $-(CH)_x-$  bridged complexes, are still few.<sup>8</sup>

During our investigation of the reactions of  $HC\equiv CCH(OH)C\equiv CH$ <sup>9</sup> with transition-metal compounds, we have isolated a novel bimetallic iridium complex from the reaction of  $HC\equiv CCH(OH)C\equiv CH$  with *cis*- $IrHCl_2(PPh_3)_3$  (**1**).<sup>10</sup> The compound is made up of two iridium centres connected by a conjugated organic bridge of ten  $sp^2$ -carbons. Interestingly, it can also be considered as two planar six-membered rings containing iridium linked by a  $-(CH)_2-$  bridge. The compound has excellent air-stability, thermo-stability and electrochemical properties. The building of stable bimetallic systems with unusual structure allowing communication is also important for practical applications.<sup>11</sup>

Treatment of *cis*- $IrHCl_2(PPh_3)_3$  (**1**) with  $HC\equiv CCH(OH)C\equiv CH$  in dichloromethane led to the formation of the dark yellow compound **2** in high yield (Scheme 1), which has been characterized by solution NMR spectroscopy and X-ray diffraction.§ The X-ray structure shown in Fig. 1 indicates that **2** has a distorted octahedral geometry around iridium. The metal atom and four carbon atoms of the penta-1,4-dien-3-ol ligand constitute a partially unsaturated five-membered ring. The metallacycle is almost planar as reflected by the small mean RMS deviation (0.1108 Å) from the least-squares plane through the five atoms Ir1, C1, C2, C3 and C4.

Five-membered ringed metallacycles are numerous, many of them act as intermediates or precursors of transition-metal-assisted reactions.<sup>12</sup> At room temperature, **2** remains nearly unchanged over 3 h in solution. To examine the reaction activity



**Scheme 1** Reagents and conditions: i)  $HC\equiv CCH(OH)C\equiv CH$ ,  $CH_2Cl_2$ , RT; ii) excess  $PBu_3$ ,  $CH_2Cl_2$ ,  $O_2$ , RT.

and improve the solubility of **2**, we have tried to replace the triphenylphosphine ligand on the iridium with tri-*n*-butylphosphine. Treatment of **2** with  $PBu_3$  in dichloromethane under nitrogen readily gave rise to a brown solution containing a mixture of **3** and another very unstable complex which could not be isolated. A green mixture was produced when the experiment was carried out under air. We have monitored the reaction and analyzed the final solution to draw the following conclusion: under air a mixture was generated after a slow and intricate process which may involve oxidative coupling and other reactions. Fortunately, we succeeded in separating the orange product **3** and another interesting green product **4**.

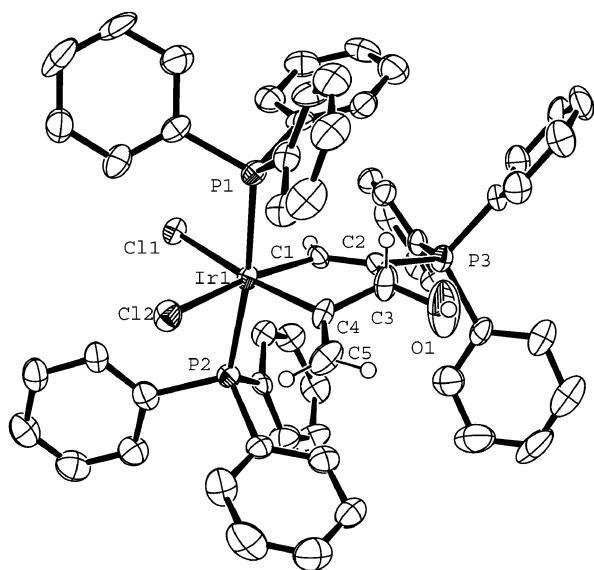
**3** could be regarded as a product formed by replacement of  $PPh_3$  with  $PBu_3$  and the dehydrogenation of  $CH(OH)$  in compound **2**. The structure of **3** has also been confirmed by X-ray diffraction§ and its ORTEP drawing is reproduced in Fig. 2. Unlike complex **2**, the five-membered metallacycle of **3** has perfect co-planarity, which is reflected by the very small mean RMS deviation (0.022 Å) from the least-squares plane through the eight atoms C1, C2, C3, C4, C5, O1, P3 and Ir1. Complex **3** also shows better air-stability and thermal stability. It remains nearly unchanged when heated at 100 °C in toluene for several hours.

The most interesting product isolated from the reaction is complex **4**. The structure of **4** has been confirmed by a single

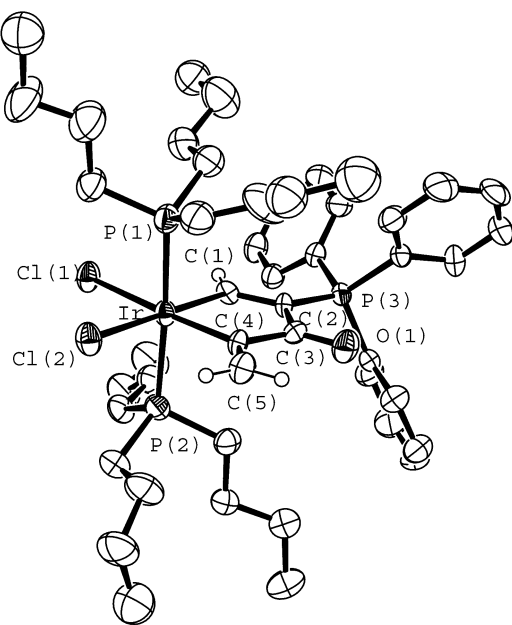
College of Chemistry and Chemical Engineering, State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, 361005, China. E-mail: hpxia@xmu.edu.cn; Fax: +86-592-2186628

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‡ Electronic supplementary information (ESI) available: Synthesis and characterization of all compounds. See DOI: 10.1039/b706900f

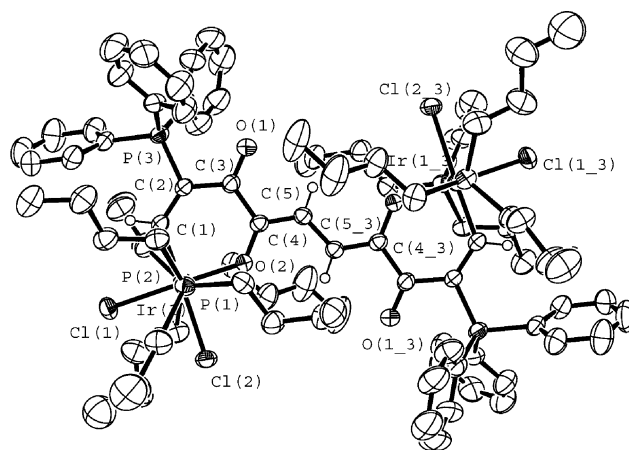


**Fig. 1** An ORTEP plot of complex **2** with thermal ellipsoids at 50% probability levels. Two  $\text{CH}_2\text{Cl}_2$  molecules and some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ir1–C1 1.986(11), Ir1–C4 2.026(11), C1–C2 1.326(16), C2–C3 1.482(18), C3–C4 1.502(18), C4–C5 1.281(18); C1–Ir1–C4 81.0(5), C1–C2–C3 115.4(11), C2–C3–C4 109.4(10), C3–C4–C5 118.3(12), C2–C3–O1 116.9(12), C4–C3–O1 119.9(13), C5–C4–Ir1 131.4(11), C3–C4–Ir1 110.5(8).



**Fig. 2** An ORTEP plot of complex **3** with thermal ellipsoids at 50% probability levels. One diethyl ether molecule and some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ir1–C1 1.965(2), Ir1–C4 2.064(2), C1–C2 1.350(2), C2–C3 1.451(3), C3–C4 1.508(3), C4–C5 1.285(4); C1–Ir1–C4 81.8(1), C1–C2–C3 115.6(2), C2–C3–C4 113.4(2), C3–C4–C5 118.3(2), C2–C3–O1 124.0(2), C4–C3–O1 122.6(2), C5–C4–Ir1 131.2(2), C3–C4–Ir1 110.5(2).

crystal X-ray diffraction study.<sup>§</sup> The ORTEP drawing is shown in Fig. 3. In this complex, the two iridium atoms are connected by a bridge consisting of a ten  $\text{sp}^2$ -carbon atom chain and a shorter bridge namely Ir1–O2–C4–C5–C5<sub>3</sub>–C4<sub>3</sub>–O2<sub>3</sub>–Ir1<sub>3</sub>. There is

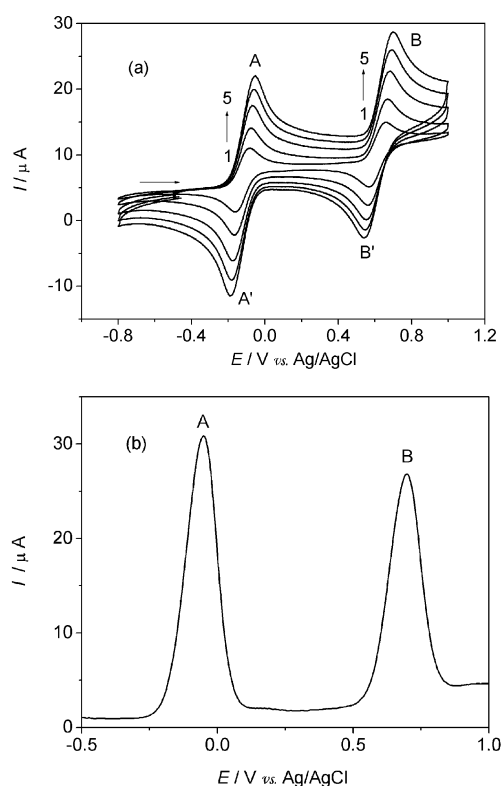


**Fig. 3** An ORTEP plot of complex **4** with thermal ellipsoids at 50% probability levels. Three  $\text{CHCl}_3$  molecules and some of the hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms:  $\_3 -x, -y + 1, -z$ . Selected bond distances [Å] and angles [°]: Ir1–C1 1.947(4), Ir1–O2 2.042(3), C1–C2 1.352(6), C2–C3 1.474(6), C3–C4 1.507(6), C4–C5 1.373(6), C3–O1 1.226(5); C5–C5<sub>3</sub> 1.436(8); C1–Ir1–O2 91.68(15), C4–O2–Ir1 128.3(3), C2–C1–Ir1 127.3(3), C1–C2–C3 127.2(4), C2–C3–C4 120.5(4), C3–C4–C5 115.2(4), C2–C3–O1 117.8(4), C4–C3–O1 121.7(4), O2–C4–C5 121.0(4), O2–C4–C3 123.8(4), C4–C5–C5<sub>3</sub> 123.4(5).

an inversion centre at the ten carbon chain linking the two Ir atoms. Atom Ir1 is linked across the inversion centre to Ir1<sub>3</sub> at  $(-x, -y + 1, -z)$ . Such a structure can also be viewed as two special six-membered iridacycles linked by a conjugated carbon bridge. Interestingly, the sixteen atoms of the rings and the bridge are almost co-planar, which is reflected by a deviation (0.0536 Å) from the RMS planes of the best fit. The exact mechanism for the formation of this novel complex is unclear at this moment.

The NMR spectroscopic data are consistent with the X-ray structure. The room-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR in  $\text{CDCl}_3$  displayed a carbonyl signal at  $\delta = 186.8$  ppm and an Ir–C signal at  $\delta = 195.2$  ppm which is significantly downfield compared with chemical shifts of typical Ir–C signals (110–140 ppm).<sup>13</sup> The signal of C5 is observed at  $\delta = 112.9$  ppm, which is comparable to those of CH groups of normal alkenes. Other signals of the bridging ligand were observed at 112.4 ppm (C2) and 156.9 ppm (C4). In the  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) spectrum, the signals attributed to Ir–CH and bridgehead CH were observed at 13.8 ppm and 6.9 ppm. In addition, the highly symmetric structure could also be confirmed by the  $^{31}\text{P}$  NMR spectrum: only two peaks at 17.5 ppm (t,  $J(\text{PP}) = 3.6$  Hz,  $\text{CPh}_3$ ) and  $-20.4$  ppm (d,  $J(\text{PP}) = 3.6$  Hz,  $\text{IrPBu}_3$ ) were observed though there are six phosphorus atoms in the structure.

The electron-transfer properties of **4** have been studied in dichloromethane containing 0.10 M  $\text{Bu}_4\text{NClO}_4$  by cyclic voltammetry. A representative voltammogram is shown in Fig. 4. Compound **4** exhibits two redox processes;  $E_{1/2}$  of the first wave (A) at  $-0.14$  V,  $\Delta E_p = 112$  mV, and  $E_{1/2}$  of the second wave (B) at  $0.61$  V,  $\Delta E_p = 130$  mV, with a scan rate of  $100 \text{ mV s}^{-1}$ . The redox peak potential differences at  $20 \text{ mV s}^{-1}$  are 80 mV (A) and 90 mV (B). The differential pulse voltammogram also shows two signals, which have identical integrated areas, consistent with two one-electron-transfer processes.<sup>14</sup> The relative peak heights  $i_{pa}/i_{pc} \approx 1$ , and peak currents are found to be linear with the square root of scan rate ( $v^{1/2}$ ) in the range from 20 to  $200 \text{ mV s}^{-1}$ , demonstrate



**Fig. 4** Cyclic (a) and differential pulse (b) voltammograms of 1 mM compound **4** (vs. Ag/AgCl). The voltammograms were recorded in  $\text{CH}_2\text{Cl}_2$  and  $\text{Bu}_4\text{NClO}_4$  (0.1 M) as the supporting electrolyte, scan rate: (1) 20, (2) 50, (3) 100, (4) 150, (5) 200  $\text{mV s}^{-1}$ .

that the two quasi-reversible one-electron processes approach that of a reversible system on the cyclic voltammetric time scale. These two oxidation waves may be attributed to the formation of  $\mathbf{4}^+$  and  $\mathbf{4}^{2+}$ , respectively. Observation of two oxidation waves for complex **4** imply that the transient intermediates of **4** are stable, probably dependent on conjugation and planarity, and there is some degree of electronic interaction between the two metal centers, due to a bridge consisting of a 10  $\text{sp}^2$  carbon atom chain or  $\text{Ir1-O2-C4-C5-C5}_3\text{-C4}_3\text{-O2}_3\text{-Ir1}_3$  as the coupling medium.

As a result of the highly conjugated and planar structure, compound **4** is quite stable to air and is also thermally stable (the sample of **4** in toluene remains nearly unchanged when heated at 100 °C in air for several hours) as well as exhibiting excellent electrochemical properties. Additionally, there are active groups like chloride on the metal atoms, which enable **4** to be linked by polydentate ligands to form a polymer. Such a polymer may be a useful precursor for mixed-valence (MV), low-dimensional conductive (LDC) and non-linear optical (NLO) materials.<sup>15</sup>

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## Notes and references

§ Crystal data for **2**:  $\text{IrCl}_2(\text{CH}=\text{C}(\text{PPh}_3)\text{CH}(\text{OH})\text{C}(\text{=CH}_2))(\text{PPh}_3)_2 \cdot 2\text{CH}_2\text{Cl}_2$ ,  $M_r = 1300.85$ , monoclinic, space group  $P2(1)/n$ ,  $Z = 4$ ,  $a = 12.833(2)$  Å,  $b = 32.704(5)$  Å,  $c = 13.692(2)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 111.703(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 5339.1(17)$  Å<sup>3</sup>; 38479 reflections, 8156

independent reflections ( $R_{\text{int}} = 0.0693$ );  $R_1 = 0.0837$ ,  $wR_2 = 0.1924$  for 619 parameters and 9407 reflections with  $[I > 2\sigma(I)]$ . Crystal data for **3**:  $\text{IrCl}_2(\text{CH}=\text{C}(\text{PPh}_3)\text{CH}(\text{OH})\text{C}(\text{=CH}_2))(\text{PPh}_3)_2 \cdot \text{Et}_2\text{O}$ ,  $M_r = 1083.18$ , monoclinic, space group  $Cc$ ,  $Z = 4$ ,  $a = 21.421(4)$  Å,  $b = 14.267(3)$  Å,  $c = 18.226(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 106.765(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 5333.5(17)$  Å<sup>3</sup>; 20742 reflections, 8087 independent reflections ( $R_{\text{int}} = 0.0294$ );  $R_1 = 0.0350$ ,  $wR_2 = 0.0897$  for 473 parameters and 9151 reflections with  $[I > 2\sigma(I)]$ . Crystal data for **4**:  $[(-\text{IrCl}_2(\text{PPh}_3)_2\text{CH}=\text{C}(\text{PPh}_3)\text{C}(\text{O})\text{CO}-)\text{=CH-}]_2 \cdot 3\text{CHCl}_3$ ,  $M_r = 2644.94$ , monoclinic, space group  $P2(1)/n$ ,  $Z = 2$ ,  $a = 14.197(2)$ ,  $b = 19.240(3)$ ,  $c = 23.412(4)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 99.442(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 6308.5(18)$  Å<sup>3</sup>. 48381 reflections, 10877 independent reflections ( $R_{\text{int}} = 0.0278$ );  $R_1 = 0.0450$ ,  $wR_2 = 0.1285$  for 557 parameters and 12382 reflections with  $[I > 2\sigma(I)]$ .

- 1 Examples of bridged ruthenium complexes: W.-Z. Chen and T. Ren, *Inorg. Chem.*, 2006, **45**, 9175–9177; G.-L. Xu, G. Zou, Y.-H. Ni, M. C. DeRosa, R. J. Crutchley and T. Ren, *J. Am. Chem. Soc.*, 2003, **125**, 10057–10065; H. P. Xia, W. F. Wu, W. S. Ng, I. D. Williams and G. Jia, *Organometallics*, 1997, **16**, 2940–2947; H. P. Xia, W. S. Ng, J. S. Ye, X.-Y. Li, W. T. Wong, Z. Lin, C. Yang and G. Jia, *Organometallics*, 1999, **18**, 4552–4557; G. Jia, H. P. Xia, W. F. Wu and W. S. Ng, *Organometallics*, 1996, **15**, 3634–3636; H. Qi, A. Gupta, B. C. Noll, G. L. Snider, Y. Lu, C. Lent and T. P. Fehlner, *J. Am. Chem. Soc.*, 2005, **127**, 15218–15227; M. C. DeRosa, C. A. White, C. E. B. Evans and R. J. Crutchley, *J. Am. Chem. Soc.*, 2001, **123**, 1396–1402; P. J. Mosher, G. P. A. Yap and R. J. Crutchley, *Inorg. Chem.*, 2001, **40**, 1189–1195; S. K. Seetharaman, M.-C. Chung, U. Englich, K. Ruhlandt-Senge and M. B. Sponsler, *Inorg. Chem.*, 2007, **46**, 561–567.
- 2 Examples of bridged iron complexes: G.-L. Xu, B. Xi, J. B. Updegraff, J. D. Protasiewicz and T. Ren, *Organometallics*, 2006, **25**, 5213–5215; R. D. Adams, B. Qu and M. D. Smith, *Organometallics*, 2002, **21**, 3867–3872; R. D. Adams, O.-S. Kwon, B. Qu and M. D. Smith, *Organometallics*, 2001, **20**, 5225–5232; N. L. Narvor, L. Toupet and C. Lapinte, *J. Am. Chem. Soc.*, 1995, **117**, 7129–7138; M. Guillemot, L. Toupet and C. Lapinte, *Organometallics*, 1998, **17**, 1928–1930; R. D. Adams, B. Qu, M. D. Smith and T. A. Albright, *Organometallics*, 2002, **21**, 2970–2978; M.-C. Chung, X. Gu, B. A. Etzenhouser, A. M. Spuches, P. T. Rye, S. K. Seetharaman, D. J. Rose, J. Zubietta and M. B. Sponsler, *Organometallics*, 2003, **22**, 3485–3494.
- 3 Examples of bridged rhenium complexes: R. Dembinski, T. Bartik, B. Bartik, M. Jaeger and J. A. Gladysz, *J. Am. Chem. Soc.*, 2000, **122**, 810–822; W. E. Meyer, A. J. Amoroso, C. R. Horn, M. Jaeger and J. A. Gladysz, *Organometallics*, 2001, **20**, 1115–1127; F. Paul, W. E. Meyer, L. Toupet, H. Jiao, J. A. Gladysz and C. Lapinte, *J. Am. Chem. Soc.*, 2000, **122**, 9405–9414.
- 4 Examples of bridged platinum complexes: N. Das, A. Ghosh, A. M. Arif and P. J. Stang, *Inorg. Chem.*, 2005, **44**, 7130–7137; P. S. Mukherjee, N. Das, Y. K. Kryschenko, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2004, **126**, 2464–2473; N. Das, P. S. Mukherjee, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2003, **125**, 13950–13951; C. J. Kuehl, S. D. Huang and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 9634–9641; J. Manna, C. J. Kuehl, J. A. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1997, **119**, 1897–1905; M. C. DeRosa, F. Al-mutlaq and R. J. Crutchley, *Inorg. Chem.*, 2001, **40**, 1406–1407; W. Kaim, B. Schwederski, A. Dogan, J. Fiedler, C. J. Kuehl and P. J. Stang, *Inorg. Chem.*, 2002, **41**, 4025–4028.
- 5 Examples of bridged iridium complexes: R. R. Tykwinski and P. J. Stang, *Organometallics*, 1994, **13**, 3203–3208; C. S. Chin, M. Kim, H. Lee, S. Noh and K. M. Ok, *Organometallics*, 2002, **21**, 4785–4793.
- 6 Examples of  $-\text{C}_x-$  bridged complexes: M. I. Bruce, P. J. Low, K. Costuas, J.-F. Halet, S. P. Best and G. A. Heath, *J. Am. Chem. Soc.*, 2000, **122**, 1949–1962; M. I. Bruce, B. G. Ellis, P. J. Low, B. W. Skelton and A. H. White, *Organometallics*, 2003, **22**, 3184–3198; G.-L. Xu, R. J. Crutchley, M. C. DeRosa, Q.-J. Pan, H.-X. Zhang, X. Wang and T. Ren, *J. Am. Chem. Soc.*, 2005, **127**, 13354–13363; H. Jiao, K. Costuas, J. A. Gladysz, J.-F. Halet, M. Guillemot, L. Toupet, F. Paul and C. Lapinte, *J. Am. Chem. Soc.*, 2003, **125**, 9511–9522; J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martín-Alvarez, F. Hampel and J. A. Gladysz, *Angew. Chem., Int. Ed.*, 2002, **41**, 1871–1876.
- 7 Examples of mixed bridged complexes: S. Frayssé, C. Coudret and J.-P. Launay, *J. Am. Chem. Soc.*, 2003, **125**, 5880–5888; T. Weyland, I. Ledoux, S. Brasselet, J. Zyss and C. Lapinte, *Organometallics*, 2000, **19**, 5235–5237.

- 8 Examples of  $-(CH)_2-$  bridged complexes: P. Yuan, S. H. Liu, W. Xiong, J. Yin, G. Yu, H. Y. Sung, I. D. Williams and G. Jia, *Organometallics*, 2005, **24**, 1452–1457; V. Guillaume, V. Mahias, A. Mari and C. Lapinte, *Organometallics*, 2000, **19**, 1422–1426; H. P. Xia, R. C. Y. Yeung and G. Jia, *Organometallics*, 1998, **17**, 4762–4768; H. P. Xia and G. Jia, *Organometallics*, 1997, **16**, 1–4; H. P. Xia, R. C. Y. Yeung and G. Jia, *Organometallics*, 1997, **16**, 3557–3560; B. A. Etzenhouser, M. D. Cavanaugh, H. N. Spurgeon and M. B. Sponsler, *J. Am. Chem. Soc.*, 1994, **116**, 2221–2222; H. H. Fox, J.-K. Lee, L. Y. Park and R. R. Schrock, *Organometallics*, 1993, **12**, 759–768; F. R. Lemke, D. J. Szalda and R. M. Bullock, *J. Am. Chem. Soc.*, 1991, **113**, 8466–8477; R. M. Bullock, F. R. Lemke and D. J. Szalda, *J. Am. Chem. Soc.*, 1990, **112**, 3244–3245; S. H. Liu, Q. Y. Hu, P. Xue, T. B. Wen, I. D. Williams and G. Jia, *Organometallics*, 2005, **24**, 769–772; S. H. Liu, H. P. Xia, T. B. Wen, Z. Zhou and G. Jia, *Organometallics*, 2003, **22**, 737–743; S. H. Liu, Y. Chen, K. L. Wan, T. B. Wen, Z. Zhou, M. F. Lo, I. D. Williams and G. Jia, *Organometallics*, 2002, **21**, 4984–4992.
- 9 E. R. H. Jones, H. H. Lee and M. C. Whiting, *J. Chem. Soc.*, 1960, 3483–3484.
- 10 L. Vaska, *J. Am. Chem. Soc.*, 1961, **83**, 756–756; S. E. Landau, K. E. Groh, A. J. Lough and R. H. Morris, *Inorg. Chem.*, 2002, **41**, 2995–3007.
- 11 S. Rigaut, C. Olivier, K. Costuas, S. Choua, O. Fadhel, J. Massue, P. Turek, J.-Y. Saillard, P. H. Dixneuf and D. Touchard, *J. Am. Chem. Soc.*, 2006, **128**, 5859–5876.
- 12 Z. Xi, K. Sato, Y. Gao, J. Lu and T. Takahashi, *J. Am. Chem. Soc.*, 2003, **125**, 9568–9569; T. Takahashi, Y. Kuzuba, F. Kong, K. Nakajima and Z. Xi, *J. Am. Chem. Soc.*, 2005, **127**, 17188–17189; C. Zhao, J. Yan and Z. Xi, *J. Org. Chem.*, 2003, **68**, 4355–4360; Q. Wang, H. Fan and Z. Xi, *Organometallics*, 2007, **26**, 775–777; Z. Xi, W.-X. Zhang, Z. Song, W. Zheng, F. Kong and T. Takahashi, *J. Org. Chem.*, 2005, **70**, 8785–8789; S. A. Johnson, F.-Q. Liu, M. C. Suh, S. Zürcher, M. Haufe, S. S. H. Mao and T. D. Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 4199–4211.
- 13 J. R. Bleeker, P. V. Hinkle, M. Shokeen and N. P. Rath, *Organometallics*, 2004, **23**, 4139–4149; K.-I. Fujita, H. Nakaguma, T. Hamada and R. Yamaguchi, *J. Am. Chem. Soc.*, 2003, **125**, 12368–12369; J. R. Bleeker and R. Behm, *J. Am. Chem. Soc.*, 1997, **119**, 8503–8511.
- 14 E. Figgemeier, E. C. Constable, C. E. Housecroft and Y. C. Zimmermann, *Langmuir*, 2004, **20**, 9242–9248.
- 15 J.-L. Fillaut, J. Perruchon, P. Blanchard, J. Roncali, S. Golhen, M. Al-lain, A. Migalsaka-Zalas, I. V. Kityk and B. Sahraoui, *Organometallics*, 2005, **24**, 687–695; C. E. Powell and M. G. Humphrey, *Coord. Chem. Rev.*, 2004, **248**, 725–756; K. Sénéchal, O. Maury, H. L. Bozec, I. Ledoux and J. Zyss, *J. Am. Chem. Soc.*, 2002, **124**, 4560–4561; N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21–38.