Dalton
Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 337

www.rsc.org/dalton

COMMUNICATION

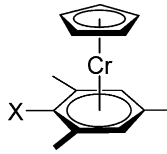
Cyclopentadienyl mesityl complexes of chromium(II) and chromium(III)†

Wen Zhou,[a] Jeffrey A. Therrien,[a] D. Lee K. Wence,[a] Emily N. Yallits,[a] Julia L. Conway,[a] Brian O. Patrick[b] and Kevin M. Smith*[a]

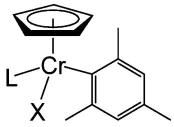
Received 15th October 2010, Accepted 19th October 2010
DOI: 10.1039/c0dt01399d

Chromium(III) mesityl complexes were synthesized by protonolysis of chromocene with 1,3-diisopropylimidazolium chloride or DBU hydrochloride, salt metathesis with MesMgBr, and single electron oxidation with iodine.

Cross-coupling catalysts based on first-row transition metals have demonstrated reactivity that is complementary to established palladium catalysts.[1] The synthesis of well-defined complexes has provided useful mechanistic details for the cross-coupling reactions of iron,[2] cobalt,[3] and nickel[4] complexes. Organochromium compounds are known to form Cr(I) species *via* reductive elimination from Cr(III).[5,6] Substituted CpCr(η^6-arene) complexes such as **A** constitute a relatively well-explored class of Cr(I) compounds.[7,8] As part of our investigation of mid-valent chromium reagents for C–C bond forming reactions,[9] we would like to communicate the synthesis of Cr(III) mesityl compounds of type **B**. The synthesis of the Cr(III) aryl halide complexes without formation of $Cr_2(\mu\text{-}X)_2$ dimers is achieved *via* salt metathesis of Cr(II) precursors with strong neutral L ligands, followed by single electron oxidation.[10]

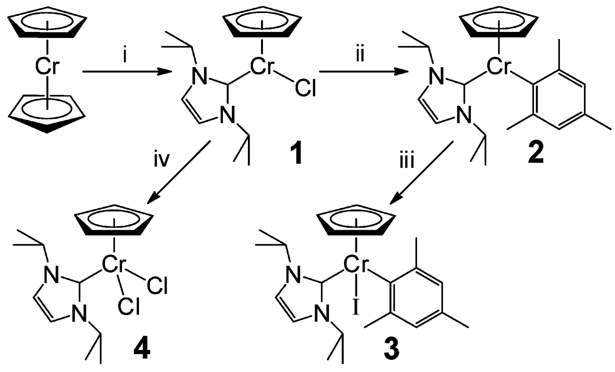


A

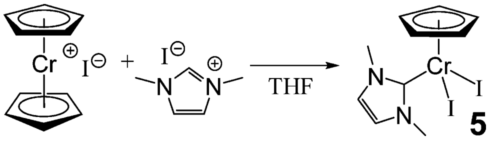


B

Reaction of chromocene with 1,3-diisopropylimidazolium chloride in THF (Scheme 1) provides bright purple CpCr(^{i}Pr-NHC)Cl (**1**) (^{i}Pr-NHC = 1,3-diisopropylimidazol-2-ylidene), analogous to the synthesis by Tilset and co-workers of the bulkier 2,4,6-$Me_3C_6H_2$ N-substituted (Mes-NHC) complex.[11] The Cr(II) chloro species **1** reacts smoothly with MesMgBr in Et_2O to give orange CpCr(^{i}Pr-NHC)Mes (**2**). Oxidation of **2** with one-half equiv. of iodine gives the deep purple Cr(III) iodo complex CpCr(^{i}Pr-NHC)(Mes)I (**3**). Oxidation with excess $PbCl_2$ provides a direct route from **1** to the Cr(III) dichloro complex CpCr(^{i}Pr-NHC)Cl_2 (**4**), as illustrated in Scheme 1. A related complex has previously been prepared by Jolly and co-workers from 1,3,4,5-tetramethylimidazol-2-ylidene and CpCrCl_2(THF).[12]



Scheme 1 *Reagents and conditions*: (i) 1,3-diisopropylimidazolium chloride, THF, 24 h; (ii) 1.2 MesMgBr, Et_2O, 2.5 h; (iii) 0.55 I_2, THF : Et_2O, 20 h; (iv) 2 $PbCl_2$, THF, 1 h.



(1)

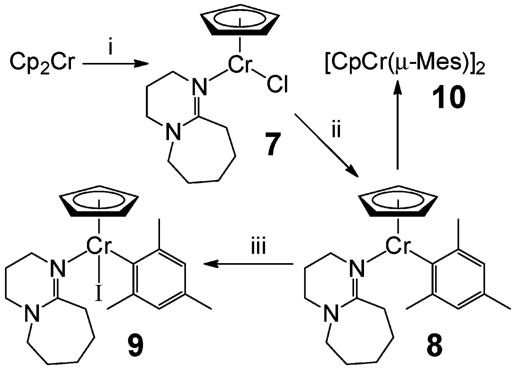
The corresponding Cr(III) diiodo complex (**5**), bearing an even less bulky N-heterocyclic carbene ligand, can be prepared by the reaction of $[Cp_2Cr]^+I^-$ with 1,3-dimethylimidazolium iodide (eqn (1)). Selective protonolysis of just one cyclopentadienyl ring is more readily achieved using the cationic Cr(III)$[Cp_2Cr]^+X^-$ precursor[13] than from neutral Cr(II) Cp_2Cr.[14] Reaction of $[Cp_2Cr]^+X^-$ with neutral β-diketones, salicylaldimines and β-ketoimines provides a convenient synthetic route to CpCr(LX)X complexes without resorting to salt metathesis. The structures of CpCr[OC(Ph)CHC(Me)O]I (**6a**), CpCr[OC_6H_4CHN(2,6-^{i}$Pr_2C_6H_3$)]I (**6b**), and CpCr[OC(Ph)CHC(Me)N(3,5-$Me_2C_6H_3$)](O_3SCF_3) (**6c**) have been determined using single-crystal X-ray crystallography (see ESI†).

Scheme 2 illustrates the synthesis of analogues of complexes **1**, **2** and **3** where the NHC has been replaced with a neutral amidine ligand.[15] Reaction of chromocene with DBU·HCl (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) in THF generates purple CpCr(DBU)Cl (**7**). Isolated **7** reacts with MesMgBr to afford CpCr(DBU)Mes (**8**), which can also be synthesized

---

[a] *Department of Chemistry, University of British Columbia Okanagan, 75 3333 University Way, Kelowna, BC, Canada. E-mail: kevin.m.smith@ubc.ca; Fax: +1 250 807 8005; Tel: +1 250 807 9933*
[b] *Department of Chemistry, University of British Columbia, Vancouver, BC, Canada*

† Electronic supplementary information (ESI) available: Full experimental details, and X-ray crystallographic data for complexes **2**, **6a**, **6b**, **6c**, **8**, **9**, and **10**. CCDC reference numbers 791384–791390. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01399d



Scheme 2 *Reagents and conditions*: (i) DBU·HCl, THF, 20 h; (ii) 1.1 MesMgBr, Et_2O, 24 h; (iii) 0.5 I_2, THF : Et_2O, 4 h.

from $CrCl_2$ by sequential addition of NaCp, 5 equiv. DBU and MesMgBr. Treatment of **8** with one-half equiv. of iodine is accompanied by a rapid colour change to a deep indigo. Recrystallization from Et_2O at −35 °C results in single-crystal X-ray quality crystals of CpCr(DBU)(Mes)I (**9**).

The violet CpCr(L)Cl complexes **1** and **7** have UV-vis bands with λ_{max} of 417 nm and 547 nm, respectively, comparable to the previously reported value of 535 nm for CpCr(Mes-NHC)Cl.[11] Replacing the chloride ligand with an aryl group shifts the band to higher energy (λ_{max} = 464 nm and 496 nm for **2** and **8**, respectively), again consistent with Tilset's CpCr(Mes-NHC)Ph compex.[11] The darker blue colour of **4** (λ_{max} = 579) is characteristic of $CpCr(L)Cl_2$ species.[11,12,16] The ^1H NMR signals of the Cr(II) and Cr(III) complexes are broad and shifted as expected for paramagnetic organochromium complexes. The downfield shifted imidazolin-2-ylidene ring protons[11] and the upfield shifted ^{i}Pr methyl groups of the ^{i}Pr-NHC complexes are perhaps the most diagnostically useful resonances observed.

The single-crystal X-ray crystal structures of **2** and **8** confirm their monomeric, two-legged piano stool geometries, with the chromium lying in the plane defined by the Cp centroid, the mesityl *ipso* carbon, and the DBU or NHC donor atom. The Cr–C(*ipso*) bond lengths of 2.0995(13) Å and 2.0931(19) Å for **2** and **8**, respectively, is similar to related Cr(II) aryl complexes.[11,17] The single-crystal X-ray crystal structure of **9** reveals a more distorted three-legged piano stool geometry with a slightly longer Cr–C(*ipso*) bond length of 2.1188(18) Å. The Cr–ligand bonds to DBU and I in **9** (Cr–N = 2.0901(15) and Cr–I = 2.7545(3)) are also significantly longer than in **8** (Cr–N = 2.0755(16)) and **6a**/**6b** (ave Cr–I = 2.6614(6)), respectively, presumably due to the increased steric repulsion in **9** (see ESI†).

Initial attempts to produce single-crystal X-ray quality crystals of **8** in Et_2O at −35 °C without additional DBU afforded black crystals of $[CpCr(\mu\text{-}Mes)]_2$ (**10**). The role of DBU in the formation of dimer **10** remains to be determined.[18] Complex **10** is more directly prepared by sequential addition of NaCp and MesMgBr to $CrCl_2$ in THF.

The molecular structure of one of the two independent dimer molecules of **10** is shown in Fig. 1. The Cr–Cr distances of 2.5496(8) and 2.5301(8) Å in $[CpCr(\mu\text{-}Mes)]_2$ are longer than those observed in $[CpCr(\mu\text{-}I)]_2$,[19] $[Cp^*Cr(\mu\text{-}Me)]_2$,[20] or $(Cp^*Cr)_2(\mu\text{-}Et)(\mu\text{-}Ph)$,[20] but are shorter than those in $[Cp^*Cr(\mu\text{-}Cl)]_2$[20] or $[CpCr(\mu\text{-}OCMe_3)]_2$.[14] The Cp_2Cr_2 core of both molecules of **10** in the unit cell are remarkably linear compared to the bent geometries observed in previously structurally characterised $[CpCr(\mu\text{-}X)]_2$ and $[Cp^*Cr(\mu\text{-}X)]_2$ complexes.[14,19,20]

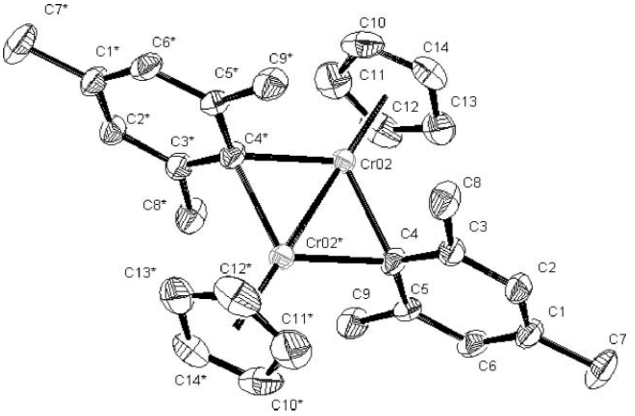


Fig. 1 Thermal ellipsoid plot (50%) of one of two independent molecules of **10** without H atoms.

The kinetics and thermodynamics of the interconversion of η^6-arene Cr(I) **A** and Cr(III) mesityl **B** are expected to vary considerably as the L and X ligands are modified. Reductive elimination from octahedral Cr(III) complexes is typically preceded by ligand loss.[5,6] The thermodynamics of oxidative addition and reductive elimination is critically dependent on the nature of the aryl–X bond.[21] With L = ^{i}Pr-NHC and X = I, complex **3** is positioned close to one end of a hypothetical continuum between **A** and **B**. We are currently developing synthetic routes to incorporate more labile neutral L donor and more strongly electron-donating anionic X ligands to explore the fundamental chemistry of relevance to cross-coupling reactivity.

We thank NSERC, CFI and UBC Okanagan for financial support, K. Cory MacLeod for assistance with the synthesis of **8** and **9** and Anita Lam for collection of single-crystal X-ray crystallographic data for **2**.

Notes and references

1 B. D. Sherry and A. Fürstner, *Acc. Chem. Res.*, 2008, **41**, 1500–1511; A. Rudolph and M. Lautens, *Angew. Chem., Int. Ed.*, 2009, **48**, 2656–2670; G. Cahiez and A. Moyeux, *Chem. Rev.*, 2010, **110**, 1435–1462.

2 A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard and C. W. Lehmann, *J. Am. Chem. Soc.*, 2008, **130**, 8773–8787; D. Noda, Y. Sunada, T. Hatakeyama, M. Nakamura and H. Nagashima, *J. Am. Chem. Soc.*, 2009, **131**, 6078–6079.

3 W. Affo, H. Ohmiya, T. Fujioka, Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, Y. Imamura, T. Mizuta and K. Miyoshi, *J. Am. Chem. Soc.*, 2006, **128**, 8068–8077.

4 G. D. Jones, J. L. Martin, C. McFarland, O. R. Allen, R. E. Hall, A. D. Haley, R. J. Brandon, T. Konovalova, P. J. Desrochers, P. Pulay and D. A. Vicic, *J. Am. Chem. Soc.*, 2006, **128**, 13175–13183; A. Castonguay, A. L. Beauchamp and D. Zargarian, *Organometallics*, 2008, **27**, 5723–5732.

5 D. Seyferth, *Organometallics*, 2002, **21**, 1520–1530; D. Seyferth, *Organometallics*, 2002, **21**, 2800–2820.

6 G. M. Whitesides and W. J. Ehmann, *J. Am. Chem. Soc.*, 1970, **92**, 5625–5640; P. W. Jolly, *Acc. Chem. Res.*, 1996, **29**, 544–551; T. Takahashi, Y. Liu, A. Iesato, S. Chaki, K. Nakajima and K. Kanno, *J. Am. Chem. Soc.*, 2005, **127**, 11928–11929; T. Agapie, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2007, **129**, 14281–14295.

7 F. H. Köhler, B. Metz and W. Strauss, *Inorg. Chem.*, 1995, **34**, 4402–4413.

8 D. S. Richeson, J. F. Mitchell and K. H. Theopold, *Organometallics*, 1989, **8**, 2570–2577; K. Jonas, *Pure Appl. Chem.*, 1990, **62**, 1169–1174; G. Wilke, H. Benn, R. Goddard, C. Krüger and B. Pfeil, *Inorg. Chim. Acta*, 1992, **198–200**, 741–748; K. Angermund, P. Betz, A. Döhring, P. W. Jolly, C. Krüger and K. U. Schönfelder, *Polyhedron*, 1993, **12**, 2663–2669; G. Bhandari, A. L. Rheingold and K. H. Theopold, *Chem.–Eur. J.*, 1995, **1**, 199–203; H. Braunschweig, T. Kupfer, M. Lutz and K. Radacki, *J. Am. Chem. Soc.*, 2007, **129**, 8893–8906.

9 K. C. MacLeod, J. L. Conway, L. Tang, J. J. Smith, L. D. Corcoran, K. H. D. Ballem, B. O. Patrick and K. M. Smith, *Organometallics*, 2009, **28**, 6798–6806.

10 K. M. Smith, *Organometallics*, 2005, **24**, 778–784.

11 M. H. Voges, C. Rømming and M. Tilset, *Organometallics*, 1999, **18**, 529–533.

12 A. Döhring, J. Göhre, P. W. Jolly, B. Kryger, J. Rust and G. P. J. Verhovnik, *Organometallics*, 2000, **19**, 388–402.

13 E. O. Fischer, K. Ulm and P. Kuzel, *Z. Anorg. Allg. Chem.*, 1963, **319**, 253–265.

14 M. H. Chisholm, F. A. Cotton, M. W. Extine and D. C. Rideout, *Inorg. Chem.*, 1979, **18**, 120–125.

15 M. P. Coles, *Dalton Trans.*, 2006, 985–1001.

16 B. Bräunlein, F. H. Köhler, W. Strauß and H. Zeh, *Z. Naturforsch. B*, 1995, **50**, 1739–1747; J. C. Fettinger, S. P. Mattamana, R. Poli and R. D. Rogers, *Organometallics*, 1996, **15**, 4211–4222.

17 A. R. Hermes, R. J. Morris and G. S. Girolami, *Organometallics*, 1988, **7**, 2372–2379; J. J. H. Edema, S. Gambarotta, F. van Bolhuis, W. J. J. Smeets, A. L. Spek and M. Y. Chiang, *J. Organomet. Chem.*, 1990, **389**, 47–59; J. L. Kersten, R. R. Kucharczyk, G. P. A. Yap, A. L. Rheingold and K. H. Theopold, *Chem.–Eur. J.*, 1997, **3**, 1668–1674; A. A. Danopoulos, D. M. Hankin, G. Wilkinson, S. M. Cafferkey, T. K. N. Sweet and M. B. Hursthouse, *Polyhedron*, 1997, **16**, 3879–3892; W. H. Monillas, G. P. A. Yap and K. H. Theopold, *Angew. Chem. Int. Ed.*, 2007, **46**, 6692–6694; A. D. Sutton, T. Nguyen, J. C. Fettinger, M. M. Olmstead, G. J. Long and P. P. Power, *Inorg. Chem.*, 2007, **46**, 4809–4814.

18 V. Lavallo and R. H. Grubbs, *Science*, 2009, **326**, 559–562.

19 M. E. Burin, M. V. Smirnova, G. K. Fukin, E. V. Baranov and M. N. Bochkarev, *Eur. J. Inorg. Chem.*, 2006, 351–356.

20 R. A. Heintz, R. L. Ostrander, A. L. Rheingold and K. H. Theopold, *J. Am. Chem. Soc.*, 1994, **116**, 11387–11396.

21 J. F. Hartwig, *Organotransition metal chemistry: from bonding to catalysis*, University Science Books, Sausalito, CA, 2010.