Unusual fragmentation of CH_2Cl_2 by an Ir(III) centre bonded to a doubly metalated Tp^{Ms} Ligand (Tp^{Ms} = hydrotris(3-mesitylpyrazol-1-yl)borate)†‡

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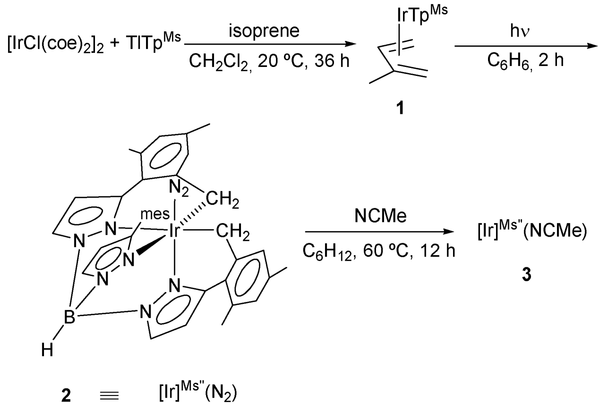
The Ir(III) compound $Tp^{Ms''}Ir(N_2)$, that contains a pentadentate, doubly metalated 3-mesityl substituted tris(pyrazolyl)borate ligand, induces the cleavage of C–H and C–Cl bonds of CH_2Cl_2 to yield a highly electrophilic chlorocarbene Ir=C(H)Cl complex.

Hydrotris(pyrazolyl)borate ligands Tp^R, where R is a 3-substituent on the pyrazolyl ring, commonly exhibit tridentate κ^3-*N,N′,N″* or κ^3-*N,N′,H* coordination,[1,2] although lower denticities, κ^2, κ^1 and even κ^0 (uncoordinated Tp^R counteranion) have also been encountered.[3] By contrast, polydentate coordination beyond κ^3 is rare, and while there are examples of κ^4 and κ^6 Tp′ binding,[4,5] the only compound that features κ^5-Tp′ coordination is a $Tp^{Ph}Ir$ derivative $Ir[\kappa^5(N,N',N'',C^{Ph},C^{Ph'})\text{–}Tp^{Ph}][\kappa^1(N^1)$-3-phenylpyrazole], that resulted from partial ligand degradation[6] during the study of the reactivity of $[IrCl(coe)_2]_2$ (coe = cyclooctene) with $TlTp^{Ph}$.

In comparison with their $Tp^{Me2}Ir$ analogues,[7] $Tp^{Ph}Ir$ compounds exhibit more versatile C–H activation chemistry,[6] including the facile, double C–H bond activation of diethyl ether to give an ethoxycarbene complex, Ir=C(H)OEt.[8] It is likely that reactivity differences among $Tp^{Me2}Ir$- and $Tp^{Ph}Ir$-compounds are largely steric in origin. Hence we have investigated the related $Tp^{Ms}Ir$ system (Ms = mesityl, *i.e.* 2,4,6-$C_6H_2Me_3$) expecting that the large cone angle (281°) and small wedge angle (7°)[1] of Tp^{Ms} would make the protective pocket around the metal tighter and result in different chemoselectivity. Herein we report a facile, photochemical double metalation of the Tp^{Ms} ligand in a reaction that gives the complex $Tp^{Ms''}Ir(N_2)$ (**2**) ($Tp^{Ms''}$ = metalated Tp^{Ms} ligand at two *ortho*-CH_3 groups of two Ms substituents). Compound **2** is a very versatile reagent for C–H bond and other C–X bond activation chemistry and effects an unusual fragmentation of CH_2Cl_2, to yield the iridium chlorocarbene $Tp^{Ms'}Ir(Cl)(=CHCl)$ ($Tp^{Ms'}$ = monometalated Tp^{Ms}), that also incorporates the cleaved H and Cl atoms in the same molecule.

A facile entry into $Tp^{Ms}Ir$ chemistry is provided by the isoprene Ir(I) complex $Tp^{Ms}Ir(\eta^4\text{-}CH_2{=}CH\text{–}C(Me){=}CH_2)$ (**1**), readily obtained by the reaction of $[IrCl(coe)_2]_2$ and $TlTp^{Ms}$,[9] in the presence of an excess of the diolefin (Scheme 1). Despite the scarcity of structurally characterized compounds of this ligand, tridentate Tp^{Ms} coordination can be suggested in **1** on the basis of a ν(B–H) infrared absorption[10a] at 2455 cm^{-1} and a $^{11}B\{^1H\}$ NMR resonance[10b] at δ −3.3. Indeed, the five-coordinate, eighteen-electron structure proposed for **1** in Scheme 1 has been demonstrated in the solid state by an X-ray structural study to be reported elsewhere.

When benzene solutions of **1** are subjected to UV irradiation for a period of 2 h, a new organoiridium(III) compound **2** forms, which contains a dimetalated tris(pyrazolyl)borate ligand, $Tp^{Ms''}$. There are no signals attributable to a hydride ligand in the ^1H NMR spectrum of **2**. Moreover, the large number of resonances found in the ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound indicates the absence of symmetry in this molecule. Two signals at 2.5 and 0.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum are diagnostic for the two chemically inequivalent iridium-bound methylene groups, and the little affected by metalation IR absorption at 2480 cm^{-1} and the $^{11}B\{^1H\}$ NMR resonance at −3.1 ppm suggest that the three pyrazolyl rings also remain N-bonded to iridium. In the IR spectrum of **2**, a sharp absorption at 2180 cm^{-1} evinces that the coordination sphere of the Ir(III) centre is completed by a molecule



Scheme 1 Formation of Ir(III) adducts containing a doubly metalated Tp^{Ms} ligand.

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‡ This article is dedicated to Prof. A. Abad on the occasion of his retirement.

of dinitrogen. For comparative purposes, in the somewhat related $\text{Tp}^{\text{Me2}}\text{Ir(Ph)}_2(\text{N}_2)$,[11] $\nu(\text{N}{\equiv}\text{N})$ appears at 2190 cm^{-1}.

Although crystals of **2** suitable for X-ray studies have proved elusive, the closely related acetonitrile adduct **3** (Scheme 1) featuring also multisignal, albeit readily interpretable NMR spectra, has been structurally authenticated by X-ray crystallography.§ Fig. 1 shows an ORTEP diagram of the molecules of **3**, and includes important bond lengths and angles.

Inspection of Fig. 1 reveals that the molecule of NCMe in **3** (and by extension that of N_2 in **2**) occupies a position *trans* with respect to one of the two pz^{Ms} rings that undergo metalation. This explains the lack of symmetry in these molecules. The six-membered metalacycles deviate considerably from planarity and are characterized by Ir–C distances that are identical within experimental error (2.08 Å). The two Ir–N bonds *trans* to the alkyls are somewhat longer (2.184(2) and 2.104(2) Å) than that *trans* to acetonitrile (2.002(2) Å). Interestingly, the metalation of the two *o*-Me groups does not appear to impose a severe strain within the Ir-ancillary ligand framework, as the angles between adjacent coordinated atoms are close to 90° (the largest deviations correspond to the N32–Ir–C310 angle of 81.9(1)° and to the N32–Ir–N41 of 98.2(1)°) while the *transoid* angles vary between 169.7(1)° and 174.8(1)°. A similar structural situation, also lacking strain, has been found in the compound $\text{Tp}^{\text{Ms}'}\text{Ru(NCMe)}_2$, that contains a singly metalated ligand.[12]

Interestingly, while benzene solutions of **2** are stable at 60 °C for hours when kept under N_2, a very fast deuteration ensues in C_6D_6 ($t_{1/2} \approx 0.3$ h), that affects the two Ir–CH_2 functionalities, as well as *all* of the *ortho*-methyl groups of the three mesityl substituents. This means that C–D bond activation of C_6D_6 takes place readily but with no detectable Ir–C_6D_5 species, probably because the chelate structure of **2** is strongly entropy favoured.

At variance with this observation, heating a CH_2Cl_2 solution of **2** at 80 °C generates cleanly the chlorocarbene complex **4** (Scheme 2), that features ^{1}H and $^{13}\text{C}\{^1\text{H}\}$ NMR signals at δ 17.66 and 270.6 ppm, respectively, attributable to a Ir=C(H)Cl unit. From the structure proposed for **4** it is apparent that a molecule of CH_2Cl_2 becomes fragmented into C(H)Cl, Cl and H units. The latter two atoms add formally to one of the Ir–CH_2 bonds, giving rise to Ir–Cl and *o*-CH_3(Ms) groups, respectively. A reasonable explanation for this result is initial C–H activation, with cleavage of one of the Ir–CH_2 bonds and formation of a dichloromethyl entity, Ir–$CHCl_2$, that subsequently undergoes α-Cl elimination.[13,17] Dihaloalkanes and related substrates are a common source of haloalkyl and of carbene and even carbyne fragments when reacted with nucleophilic mononuclear[13–16] and binuclear[17] compounds, and chloro carbenes of the type M = C(R)Cl are well-known derivatives.[18] However, the parent C(H)Cl ligand is hardly known.[19] Moreover, we are unaware of a fragmentation of the kind giving origin to **4**.

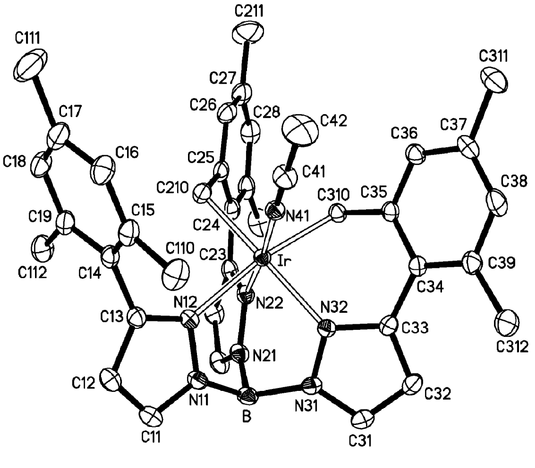
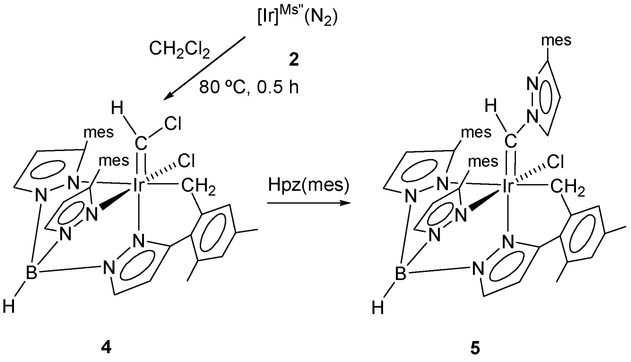


Fig. 1 ORTEP plot of **3** (hydrogen atoms omitted for clarity; thermal ellipsoids are at the 20% probability level). Selected bond lengths (Å) and angles (°): Ir–N(12) 2.184(2), Ir–N(22) 2.002(2), Ir–N(32) 2.104(2), Ir–C(210) 2.080(3), Ir–C(310) 2.086(3), Ir–N(41) 1.976(2), N(22)–Ir–N(41) 174.8(1), N(12)–Ir–C(310) 170.6(1), N(32)–Ir–C(210) 169.7(1), N(12)–Ir–N(22) 85.1(1), N(12)–Ir–N(32) 88.7(1), N(22)–Ir–N(32) 86.9(1), N(32)–Ir–C(310) 81.9(1), N(22)–Ir–C(210) 83.4(1).



Scheme 2 Formation of heteroatom-stabilized carbenes **4** and **5**.

Despite the seemingly protective pocket created around the iridium centre by the tetradentate $\text{Tp}^{\text{Ms}'}$ ligand, the carbene carbon atom is highly susceptible to nucleophilic attack and reacts with adventitious water forming a related hydroxycarbene species, to be reported later in full. This has prevented isolation of analytically pure samples of **4**. Moreover, treatment of this species with 1 equiv. of 3-mesitylpyrazole, Hpz(Ms), generates (quantitatively by ^{1}H NMR) the pyrazolyl-substituted carbene complex **5** (Scheme 2). As found for **4**, the carbene functionality of **5** exhibits characteristic ^{1}H (δ 15.34) and $^{13}\text{C}\{^1\text{H}\}$ resonances (231.5 ppm). X-ray studies provide unequivocal structural evidence,§ and show a somewhat distorted, but essentially octahedral geometry (Fig. 2). The angles between ligands in *cis* are close to the ideal 90° value, the largest deviation being naturally associated with the metalated CH_2 (Ms) and its corresponding pyrazolyl ring (C312–Ir–N32 angle of 80.1(1)°). The Ir–N22 distance, *trans* to the Ir–CH_2 group at 2.187(4) Å is longer than the other two (Ir–N12 = 2.083(4) Å; Ir–N32 = 2.102(3) Å), reflecting the higher *trans* influence of the sp^3 alkyl carbon, as compared to the carbene and the chloride ligands. The Ir=C bond length of 1.905(4) Å (Ir–C413) is normal[6–8] and, as expected, significantly shorter than the Ir–CH_2 separation of 2.066(4) Å (Ir–C312).

In summary, with the synthesis of complex **2** and its related NCMe adduct **3**, we have demonstrated that the Tp^{Ms} ligand can become pentadentate by means of the metalation of two *ortho*-CH_3 groups of the 3-mesityl substituents, without imposing severe structural tension. With this finding we have gained a facile, convenient entry into C–H (and other C–X) bond activation chemistry. The bulkiness of this ligand raises reasonable expectations for novel chemical reactivity and structures, which would be the subject of forthcoming publications from our laboratories.

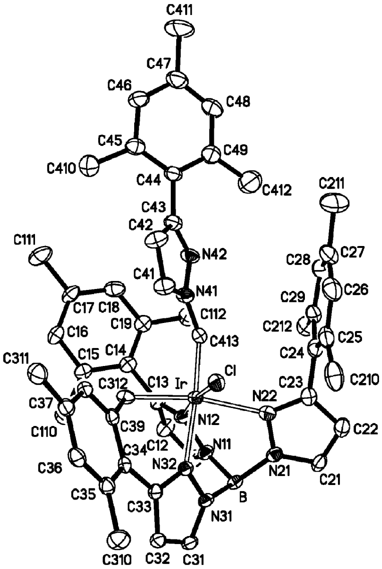


Fig. 2 ORTEP plot of **5** (hydrogen atoms omitted for clarity; thermal ellipsoids are at the 40% probability level). Selected bond lengths (Å) and angles (°): Ir–N(12) 2.083(4), Ir–N(22) 2.187(4), Ir–N(32) 2.102(3), Ir–C(413) 1.905(4), Ir–C(312) 2.066(4), Ir–Cl 2.336(1), N(12)–Ir–Cl 173.6(1), N(22)–Ir–C(312) 168.2(2), N(32)–Ir–C(413) 174.6(1), N(32)–Ir–C(312) 80.1(1), N(12)–Ir–N(22) 87.6(1), N(12)–Ir–N(32) 85.1(1), N(22)–Ir–N(32) 88.2(1).

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Notes and references

§ Crystallographic data for: **3**: $C_{38}H_{41}BIrN_7$, M = 798.79, monoclinic, space group $P2_1/c$, a = 14.3166(13), b = 13.5819(12), c = 19.9953(18) Å, β = 106.611(2)°, V = 3725.8(6) Å^3, T = 297(2) K, Z = 4, μ = 3.619 mm^{-1}, 67158 reflections measured, 10876 independent, R_{int} = 0.0454, $R_1[I > 2\sigma(I)]$ = 0.0301, wR_2(all data) = 0.0823. CCDC 610650. **5**: $C_{49}H_{53}BClIrN_8$, M = 992.45, tetragonal, space group $I\bar{4}2d$, a = 22.4579(6), c = 35.6656(18) Å, V = 17988.2(11) Å^3, T = 173(2) K, Z = 16, μ = 3.072 mm^{-1}, 71652 reflections measured, 9059 independent, R_{int} = 0.0631, $R_1[I > 2\sigma(I)]$ = 0.0305, wR_2(all data) = 0.0578. CCDC 610651. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608293a

1 For a comprehensive review of Tp^R complexes see: S. Trofimenko, *Scorpionates; The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999. Earlier reviews: S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943; G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291. See also: *Polyhedron*, 2004, **23**, 197 issue dedicated to M–Tp′ compounds.

2 J. C. Calabrese, P. J. Domaille, J. S. Thompson and S. Trofimenko, *Inorg. Chem.*, 1990, **29**, 4429; A. Kremer-Aach, W. Kläui, R. Bell, A. Strerath, H. Wunderlich and D. Mootz, *Inorg. Chem.*, 1997, **36**, 1552.

3 U. E. Bucher, A. Currao, R. Nesper, H. Rüegger, L. M. Venanzi and E. Younger, *Inorg. Chem.*, 1995, **34**, 66; H. F. Malbosc, P. Kalck, J.-C. Daran and M. Etienne, *J. Chem. Soc., Dalton Trans.*, 1997, 271; M. Paneque, S. Sirol, M. Trujillo, E. Gutiérrez-Puebla, A. Monge and E. Carmona, *Angew. Chem., Int. Ed.*, 2000, **39**, 218; M. Paneque, S. Sirol, M. Trujillo, E. Gutiérrez-Puebla, A. Monge, E. Carmona, C. Ruiz, H. F. Malbosc, C. Serra-Le Berre, P. Kalck, M. Etienne and J.-C. Daran, *Chem.–Eur. J.*, 2001, **7**, 3869.

4 A. J. Amoroso, J. C. Jeffery, P. L. Jones, J. A. McCleverty, E. Psillakis and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1994, 2751; A. J. Amoroso, J. C. Jeffery, P. L. Jones, J. A. McCleverty, L. Rees, A. L. Rheingold, Y. Sun, J. Takats, S. Trofimenko, M. D. Ward and G. P. A. Yap, *J. Chem. Soc., Chem. Commun.*, 1995, 1881; P. L. Jones, K. L. V. Mann, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *Polyhedron*, 1997, **16**, 2435; A. L. Rheingold, B. S. Haggerty, L. M. Liable-Sands and S. Trofimenko, *Inorg. Chem.*, 1999, **38**, 6306; M. C. Keyes, V. G. Young, Jr. and W. B. Tolman, *Organometallics*, 1996, **15**, 4133; Y. Takahashi, S. Hikichi, A. Akita and Y. Moro-oka, *Organometallics*, 1999, **18**, 2571.

5 N. Kitajima, M. Osawa, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1991, **113**, 8952; Y. Takahashi, S. Hikichi, M. Akita and Y. Moro-oka, *Chem. Commun.*, 1999, 1491; R. Krentz, Ph. D. Dissertation, University of Alberta, Edmonton, 1989.

6 C. Slugovc, K. Mereiter, S. Trofimenko and E. Carmona, *Chem. Commun.*, 2000, 121; C. Slugovc, K. Mereiter, S. Trofimenko and E. Carmona, *Helv. Chim. Acta*, 2001, **84**, 2868.

7 E. Carmona, M. Paneque and M. L. Poveda, *Dalton Trans.*, 2003, 4002; E. Carmona, M. Paneque, L. L. Santos and V. Salazar, *Coord. Chem. Rev.*, 2005, **249**, 1729.

8 C. Slugovc, K. Mereiter, S. Trofimenko and E. Carmona, *Angew. Chem., Int. Ed.*, 2000, **39**, 2158.

9 A. L. Rheingold, C. B. White and S. Trofimenko, *Inorg. Chem.*, 1993, **32**, 3471.

10 (*a*) M. Akita, K. Ohta, Y. Takahashi, S. Hikichi and Y. Moro-oka, *Organometallics*, 1997, **16**, 4121; (*b*) T. O. Northcutt, R. J. Lachicotte and W. D. Jones, *Organometallics*, 1998, **17**, 5148.

11 E. Gutiérrez-Puebla, A. Monge, M. C. Nicasio, P. J. Pérez, M. L. Poveda and E. Carmona, *Chem.–Eur. J.*, 1998, **4**, 2225.

12 C. Pariya, C. D. Incarvito, A. L. Rheingold and K. H. Theopold, *Polyhedron*, 2004, **23**, 439.

13 H. B. Friedrich and J. R. Moss, *Adv. Organomet. Chem.*, 1991, **33**, 235.

14 W. L. Olson, D. A. Nagaki and L. F. Dahl, *Organometallics*, 1986, **5**, 630; T. Yoshida, T. Ueda, T. Adachi, K. Yamamoto and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, 1985, 1137; T. B. Marder, W. C. Fultz, J. C. Calabrese, R. L. Harlow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1543.

15 H. Werner, M. Laubender, R. Wiedemann and B. Windmüller, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1237; M. Oliván and K. C. Caulton, *Chem. Commun.*, 1997, 1733.

16 F. J. Lalor, T. J. Desmond, G. M. Cotter, C. A. Shanahan, G. Ferguson, M. Parvez and B. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1995, 1709; A. J. Vetter and W. D. Jones, *Polyhedron*, 2004, **23**, 413.

17 D. G. Harrison and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1986, 285; M. A. Ciriano, M. A. Tena and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, 1992, 2123; C. Tejel, M. A. Ciriano, L. A. Oro, A. Tiripicchio and F. Ugozzoli, *Organometallics*, 2001, **20**, 1676; G. E. Ball, W. R. Cullen, M. D. Fryzuk, B. R. James and S. J. Rettig, *Organometallics*, 1991, **10**, 3767; J. J. Brunet, X. Couillens, J. C. Daran, O. Diallo, C. Lepetit and D. Neibecker, *Eur. J. Inorg. Chem.*, 1998, **3**, 349.

18 P. J. Brothers and W. R. Roper, *Chem. Rev.*, 1988, **88**, 1293.

19 S. V. Hoskins, C. E. F. Rickard and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1984, 1002; R. G. Clark, W. R. Roper and A. H. Wright, *J. Organomet. Chem.*, 1982, **236**, C7.