Room temperature benzene C–H activation by a new [PSiP]Ir pincer complex[†]

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Received (in Berkeley, CA, USA) 10th July 2008, Accepted 6th September 2008 First published as an Advance Article on the web 23rd September 2008 DOI: 10.1039/b811811f

The synthesis and reactivity of coordinatively unsaturated Rh and Ir complexes supported by the new bis(phosphino)silyl pincer ligand $[\kappa^3-(2-Cy_2PC_6H_4)_2SiMe]^-$ ([Cy-PSiP]⁻) are reported, including the first example of facile, room temperature intermolecular arene C–H bond activation mediated by a silyl pincer complex.

The metal-mediated activation and functionalization of hydrocarbon C-H bonds represent a fundamental goal in modern chemistry.¹ Significant progress has been made in this area during the past twenty years, particularly with respect to the discovery of late transition metal complexes that can cleave hydrocarbon C-H bonds under mild conditions. In this context, much attention has been given to iridium complexes, due in part to the pioneering work of Bergman^{1c,2} and Graham,³ who independently showed that photochemically generated Cp*IrL (Cp* = η^5 -C₅Me₅, L = R₃P or CO) species can oxidatively add alkane and arene C-H bonds. Subsequent work also showed that Ir(III) species such as $Cp^{*}(PMe_{3})IrMe^{+}X^{-}$ (X = OTf, $B(C_{6}F_{5})_{4}$) can undergo thermal intermolecular C-H bond activation reactions under mild conditions.⁴ Innovations in ancillary ligand design have figured prominently in the continued advancement of iridiummediated C-H bond activation chemistry. Notably, the use of phosphine-based 'PCP' pincer ligands has enabled the development of cyclometalated [PCP]Ir ([PCP] = κ^3 -2,6-(^tBu₂- $PCH_2_2C_6H_3$ complexes that are able to mediate the catalytic dehydrogenation of alkanes.⁵ In this regard, the identification of new ancillary ligation strategies for promoting metal-mediated C-H bond activation represents an important challenge, as such discoveries can serve as the starting point for the rational development of efficient catalytic hydrocarbon functionalization chemistry.

In this contribution, we report new coordinatively unsaturated group 9 pincer complexes supported by the bis(phosphino)silyl ligand [κ^3 -(2-Cy₂PC₆H₄)₂SiMe]⁻ ([Cy-PSiP]⁻), including the first example of facile, room temperature intermolecular C–H bond activation mediated by a silyl

pincer complex. Although metal-silicon chemistry is wellprecedented,⁶ little attention has been given to the incorporation of silyl donor fragments into the framework of a preformed tridentate ancillary ligand. A notable exception is the work of Stobart and co-workers,⁷ who have reported late transition metal complexes featuring multidentate phosphinosilvl ligands. As well, Tilley and co-workers⁸ have recently reported late metal complexes featuring a rigid, tridentate NSiN ligand framework, including the high temperature (120 °C) dehydrogenative silvlation of arenes catalyzed by [NSiN]Ir(III) species; notably, no isolable Ir products of C-H bond activation were reported in this study. While it has been proposed that the incorporation of strongly electron donating and trans-labilizing silyl groups into pincer ligand architectures may promote the formation of coordinatively unsaturated complexes that can mediate aggressive bond activation chemistry, beyond the aforementioned report by Tilley and co-workers,^{8b} the utility of such complexes in C-H bond activation processes has not been demonstrated.

We have recently reported on the synthesis and catalytic utility of cyclometalated [Ph-PSiP]⁻ ([Ph-PSiP]⁻ = $[\kappa^{3}-(2-Ph_{2}PC_{6}H_{4})_{2}SiMe]^{-})$ platinum group metal complexes.⁹ In an attempt to access more electron rich metal species, we undertook the synthesis of the dicyclohexylphosphino derivative, [Cy-PSiP]⁻. The parent tertiary silane, [Cy-PSiP]H (1) was obtained in 69% isolated yield by lithiation of $2-Cy_2PC_6H_4Br$ with "BuLi, followed by *in situ* treatment with 0.5 equiv. of MeSiHCl₂. In contrast to the formation of [Ph-PSiP]RhHCl(PPh3) upon treatment of [Ph-PSiP]H with one equiv. of Rh(PPh₃)₃Cl,⁹ employing 1 under similar conditions resulted in quantitative (by ³¹P NMR spectroscopy) formation of the coordinatively unsaturated complex [Cy-PSiP]RhHCl (2) with liberation of three equiv. of PPh₃ (Fig. 1). Alternatively, 2 was also readily prepared (85%) isolated yield) by the reaction of 1 with half an equiv. of $[Rh(COE)_2Cl]_2$ (COE = η^2 -cyclooctene). The Ir analog [Cy-PSiP]IrHCl (3) was prepared under similar reaction conditions (75% isolated yield), employing half an equiv. of $[Ir(COE)_2Cl]_2$. Both 2 and 3 exhibit C_s -symmetry in solution (³¹P NMR spectroscopy) and the X-ray crystal structures of both $2 \cdot (OEt_2)_2^{10}$ and $3 \cdot (OEt_2)_2^{10}$ (Fig. 1)‡ confirm the formation of structurally analogous, Cs-symmetric five-coordinate complexes in which the pincer phosphine donors are trans-oriented. The geometry at the metal center in both complexes can be described as distorted square-based pyramidal, with Si occupying the apical coordination site.¹¹ Notably, both

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[†] Electronic supplementary information (ESI) available: Experimental details and characterization data, including crystallographic data for 2 (OEt₂)₂ and 3 (OEt₂)₂. CCDC 693921–693922. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/ b811811f



Fig. 1 Synthesis of 2 and 3. The crystallographically determined structure of $3\cdot(OEt_2)_2$, shown with 50% displacement ellipsoids; selected hydrogen atoms and the diethyl ether solvates have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for $3\cdot(OEt_2)_2$ (and $2\cdot(OEt_2)_2$): M–Cl 2.414(1) (2.4109(6)); M–P 2.2980(9) (2.3017(5)); M–Si 2.274(1) (2.2616(7)); M–H1 1.55 (1.51(3)); P–M–P 166.07(4) (165.59(2)); Cl–M–H1 160.6(18) (162.5(12)); Cl–M–Si 130.64(5) (131.68(2)); Si–M–H1 68.7(18) (65.8(12)).

complexes feature relatively short Si–H1 distances (M = Rh, 2.14(3) Å; M = Ir, 2.24(5) Å) that fall within the sum of the van der Waals radii (3.4 Å). These distances are longer than those typically observed for σ -silane complexes, but do fall within the range indicative of significant Si–H interaction.¹² No evidence of such an Si–H interaction is observed in solution, as indicated by the small ${}^{2}J_{SiH}$ (<10 Hz) measured for **2** and **3**.¹³

The addition of MeLi (1.6 M in Et₂O) to a room temperature benzene solution of 3 resulted in quantitative conversion to [Cy-PSiP]IrH(Ph) (4) with concomitant evolution of methane (Scheme 1), as indicated by ³¹P and ¹H NMR analysis of the reaction mixture, which revealed a new Ir-H resonance at -11.75 ppm (t, ${}^{2}J_{PH} = 17$ Hz) as well as resonances consistent with an Ir-Ph ligand. Spectroscopic analysis of the reaction mixture immediately upon addition of MeLi revealed the formation of 4, methane, as well as an intermediate Ir-H species 5, which we tentatively assign as [Cy-PSiP]IrH(Me). The formation of 4 is complete over the course of an hour at room temperature. Compound 4 arises from the Ir-mediated C-H bond activation of benzene. Consistent with this scenario, when the addition of MeLi was performed in benzene- d_6 solution, deuterium incorporation was observed at both the Ir-H and Ir-Ph positions to yield $4-d_6$. To further confirm this assignment, 4 was independently generated by the reaction of 3 with PhLi.

Analogous to the reactivity observed with benzene, the addition of MeLi to a room temperature toluene solution of **3** resulted in the formation of arene C–H activation products (**6a,b**), as indicated by the formation of two new Ir–H species



Scheme 1 C-H Bond activation chemistry arising from 3.

(*ca.* 3 : 2 ratio; δ^{-1} H = -11.70, -11.82; δ^{-31} P = 57.1, 57.0), consistent with the formation of a mixture of *para*- and *meta*-tolyl isomers (Scheme 1).¹⁴ ²H NMR analysis of **6a,b**-*d*₈ (prepared *via* C–D activation of toluene-*d*₈) revealed deuterium incorporation at the Ir–H and Ir–aryl positions, as well as two aryl–Me resonances (2.03 and 2.36 ppm, *ca.* 3 : 2 ratio). No evidence for benzylic C–H bond activation was observed.

In an effort to understand the reactivity of 3 with MeLi in the absence of arene solvents, the room temperature methylation of **3** was examined in cyclohexane- d_{12} . ¹H NMR analysis of the reaction mixture upon addition of MeLi indicated the quantitative consumption of 3 and the formation of methane, accompanied by the appearance of broad aromatic and [Cy-PSiP]-cyclohexyl resonances, as well as a broad Ir-H resonance centered near -11.3 ppm. The ³¹P NMR spectrum of this mixture exhibited a complex multiplet centered near 56.2 ppm, and both the ¹H and ³¹P NMR spectral features did not vary significantly between -90-90 °C (methylcyclohexane- d_{14}). While the observation of a new Ir-H resonance may point to the formation of a cyclometalated variant of [Cy-PSiP]Ir, we have thus far not been able to identify unambiguously the product of this reaction. However, the addition of an excess of benzene to this reaction mixture resulted in the quantitative formation of 4.

Facile intermolecular arene exchange was found to occur with 4.¹⁵ Upon standing in benzene- d_6 for 14 h at room temperature or 1 h at 70 °C, 4 was cleanly converted to 4- d_6 with liberation of benzene (¹H NMR analysis); ²H NMR analysis confirmed that deuterium incorporation occurred exclusively at the Ir–H and Ir–Ph positions (Scheme 1). Similarly, in toluene solution, 4 was transformed cleanly into **6a,b** with liberation of benzene upon heating at 70 °C for 1 h.

By comparison with the Ir system, no intermolecular C–H bond activation was observed for [Cy-PSiP]Rh species. Thus far, we have observed that the reaction of **2** with MeLi in either alkane or arene solvents leads to the quantitative formation of the same as-yet-unidentified Rh-containing product **7** ($\delta^{31}P = 62.9$, ${}^{1}J_{RhP} = 162$ Hz), with concomitant elimination of methane. Compound **7** features broadened ${}^{1}H$ and ${}^{31}P$ NMR resonances that are not resolved between -90-100 °C (methylcyclohexane- d_{14}), and no indication of a Rh–H resonance was observed (${}^{1}H$ NMR analysis) in this temperature range.

In summary, we have prepared coordinatively unsaturated Rh and Ir complexes supported by the new bis(phosphino)silyl pincer ligand [Cy-PSiP]⁻, and have demonstrated for the first time that Ir silyl pincer complexes can mediate intermolecular aryl C–H bond activation processes, including arene exchange, under mild conditions. Silyl pincer ligation represents a new platform for hydrocarbon activation studies, as well as for other aggressive bond activation chemistry that requires an electron-rich metal center. Further studies aimed at elucidating the mechanism of C–H bond activation by [Cy-PSiP]Ir species, as well as expanding the scope of E–H (E = main group element) bond activation mediated by [PSiP]-ligated complexes, are currently underway.

We are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada and Dalhousie University for their support of this work. We also thank Dr M. Lumsden (Atlantic Region Magnetic Resonance Center, Dalhousie) for assistance in the acquisition of NMR data.

Notes and references

‡ Crystallographic data in CIF format have been deposited for **2**·(**OEt**₂)₂ (CCDC 693922) and **3**·(**OEt**₂)₂ (CCDC 693921). Selected crystal data for **2**·(**OEt**₂)₂ (C₄₅H₇₆ClO₂P₂RhSi, 877.45 g mol⁻¹): a = 17.141(2) Å, b = 15.052(2) Å, c = 18.351(2) Å, V = 4734.7(8) Å³, space group = *Pnma* (orthorhombic), Z = 4, $T = 193(\pm 2)$ K, independent reflections = 5619 ($R_{int} = 0.0272$), GOF = 1.093, $R_1 = 0.0279$ ($F_o^2 > 2\sigma(F_o^2)$), w $R_2 = 0.0766$ (all data); selected crystal data for **3**·(**OEt**₂)₂ (C₄₅H₇₆ClTO₂P₂Si, 966.74 g mol⁻¹): a = 17.181(1) Å, b = 15.041(1) Å, c = 18.333(1) Å, V = 4737.6(6) Å³, space group = *Pnma* (orthorhombic), Z = 4, $T = 193(\pm 2)$ K, independent reflections = 4684 ($R_{int} = 0.0679$), GOF = 1.049, $R_1 = 0.0278$ ($F_o^2 > 2\sigma(F_o^2)$), w $R_2 = 0.0663$ (all data).

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