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Note

Ligand metalation in an iridiumtris(diisopropylphosphinomethyl)borato complex: Synthesis, molecular structure and reactivity

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Dedicated to Professor Dr. h.c. mult. W. A. Herrmann on the occasion of his 60th birthday.

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ABSTRACT

The reaction of [IrCl(dmso)$_3$] with trisphosphinomethylborato ligand Li(THF){PhB(CH$_2$P^{i}Pr$_2$)$_3$} at room temperature results in intramolecular C–H activation of one of the ^{i}Pr substituents affording two diastereomers of cyclometalated iridium(III) complex [Ir(H)(dmso){PhB(CH$_2$P^{i}Pr$_2$)$_2$(CH$_2$P^{i}PrCHMeCH$_2$)}] (**1**) in high yield in approximately equimolar ratio. NMR spectroscopic characterization indicates that only the diastereomers with the hydride ligand in *cis* position with respect to the metalacyclic phosphorous atom are formed as confirmed by single crystal X-ray diffraction. Facile ring opening with H_2 at room temperature gives dihydride [Ir(H)$_2$(dmso){PhB(CH$_2$P^{i}Pr$_2$)$_3$}] (**2**). However, C–H activation of benzene was not observed.

1. Introduction

The activation of C–H bonds by transition metal complexes is of major interest owing to its potential for hydrocarbon functionalization [1]. While intramolecular C–H oxidative addition to metal centers, such as the *ortho*-metalation of coordinated arylphosphines, was discovered more than 40 years ago and turned out to be quite common, advances in intermolecular C–H activation are much more recent and the topic remains a challenging goal [2]. Particularly intermolecular alkane and arene C–H activation with derivatives of cyclopentadienyl (Cp) and trispyrazolylborato (Tp) iridium(I) complexes was the subject of numerous mechanistic studies [3,4]. Although both monoanionic 6-electron donor ligands are generally considered similar, distinct differences, such as the stronger electron donating ability of the soft cylopentadienyl derivatives and the much higher propensity of the hard Tp ligands for η^2 coordination, have been pointed out in the past [4,5].

Recently, Tilley, Peters, and Nocera have introduced tripodal, monoanionic trisphosphinomethylborato ligands of the type {PhB(CH$_2$PR$_2$)$_3$}$^-$ ({PhBP$^R_3$}$^-$; R = Ph, ^{i}Pr). [6] According to CO stretching vibrations in carbonyl complexes, strong electron donation renders this ligand type comparable with electron rich Cp ligands. On the other hand, facile changes in hapticity (η^2/η^3) as in Tp complexes have been observed, as well [6c,7]. In the past years, {PhBP$^R_3$}-type ligands were utilized in late transition metal chemistry for various applications, e.g., for the stabilization of terminal iridium silylene and late 3*d* metal imido and nitride complexes [6a,8,9], dinitrogen activation [10], or in single source precursors for chemical vapor deposition (CVD) [11]. However, while the activation of H–H and Si–H bonds with M{PhBP$^R_3$} (M = Ir, Rh) fragments has been studied before [7], not much emphasis was put on C–H activation.

In this context we were interested if Ir{PhBP$^R_3$} fragments can be used for intermolecular hydrocarbon activation. Intermolecular, allylic C–H activation was observed in the reaction of IrCl(olefin)$_n$ (olefin = cyclooctene, propene) with Li(THF){PhBP$^R_3$} (R = Ph, ^{i}Pr) [7,12]. However, for R = Ph olefin reductive elimination affords facile and irreversible *ortho*-metalation. Since trialkylphosphine cyclometalation is much less common and more likely to be reversible given the tendency for iridium to activate C–H bonds in the order aryl >1° > 2° ≫ 3°, we examined if the use of the {PhBP$^{iPr}_3$} ligand permits intermolecular aromatic C–H activation [1a,13].

2. Results and discussion

The reaction of [IrCl(dmso)$_3$] with Li(THF){PhBP$^{iPr}_3$} affords two compounds by NMR spectroscopy in approximately equimolar ratio in high overall yield (Scheme 1). Repeated fractional crystal-

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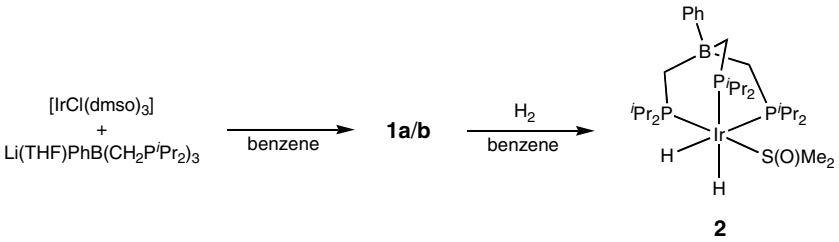

Scheme 1. Synthesis of Ir{PhBP$^{iPr}_3$} complexes.

lization allowed isolation of one complex, albeit in very low yield due to their close solubility. NMR spectroscopic characterization and combustion analysis of the product mixture are in agreement with the formation of two diastereomers of cyclometalated [Ir(H)(dmso){PhB($CH_2P^iPr_2$)$_2$(CH_2P^iPrCHMeCH_2)}] (**1**). Both isomers feature three signals in the ^{31}P NMR spectrum, respectively, indicating low symmetry around the metal centers. The distinct upfield shift of one ^{31}P NMR signal (**1a**: −42.5 ppm/**1b**: −31.0 ppm) is characteristic of four-membered phosphacycles as in cyclometalated phosphine ligands [14]. In the ^{1}H NMR spectrum one hydridic signal is observed, respectively, as a doublet of triplets with one large *trans* $^2J_{HP}$ (**1a**: 121.5 Hz/**1b**: 119.9 Hz) and a small *cis* $^2J_{HP}$ coupling constant (**1a**: 12.8 Hz/**1b**: 11.6 Hz). In the alkyl region a complicated pattern is observed with multiple superimposed signals for the *iso*-propyl groups owing to the low symmetry of the complex. However, two sharp singlet signals for each complex, respectively, can be assigned to a sulfur-bound dmso ligand indicating hindered rotation about the Ir–S bond.

With respect to the two stereocenters in complex **1**, the metal center and the metalacyclic methyne carbon atom (C16, Fig. 2), four diastereomers could be possible products (Fig. 1) if idealized local C_{3v} symmetry for the {BP_3} backbone is assumed [15]. Selectively decoupled ^{1}H-{^{31}P} NMR spectra indicate, that the hydride ligands in the diastereomers obtained are *not* located *trans* to the metalacyclic phosphorous atoms but to the ones with ^{31}P NMR signals at −10.3 ppm (**1a**) and −12.7 ppm (**1b**), respectively. Therefore, structures **C** and **D** can be excluded by NMR spectroscopy, rendering structures **A** and **B**, and their respective enantiomers, the isomers observed for **1**.

The molecular structure of diastereomer **1a**, which is less soluble in hydrocarbon solvents, could be derived by single crystal X-ray diffraction (Fig. 2). The structure, which was solved in the centrosymmetric space group $P2_1/n$, features *facial* coordination of the trisphosphinoborato ligand with one *iso*-propyl substituent cyclometalated to give a four-membered phophametalacycle. Furthermore, an *S*-bound dmso ligand is located *trans* to the metalacyclic phosphorous atom P2. The remaining hydride was not located on the electron density map but calculated at the remaining coordination site *trans* to P1, in agreement with the large Ir–P1 distance (2.426(1) Å) due to the strong hydride ligand *trans*-influence. Therefore, the stereochemistry of **1a** is represented by structure **A** (Fig. 1). The three P–Ir–P angles are close to 90°, as typically observed for trisphosphinoborato ligands [12]. Major distortion from ideal octahedral geometry arises from ring strain within the four-membered metalacycle (P2–Ir–C17: 69.9(1)°) and steric repulsion of the dmso ligand with P^iPr_2 groups resulting in large S–Ir–P1 (100.27(4)°) and S–Ir–P3 (106.22(4)°) *cis* angles and a small S–Ir–P2 (159.41(4)°) *trans* angle. The metalacycle is almost perfectly planar with a sum of bond angles within the four membered ring of 359.3°.

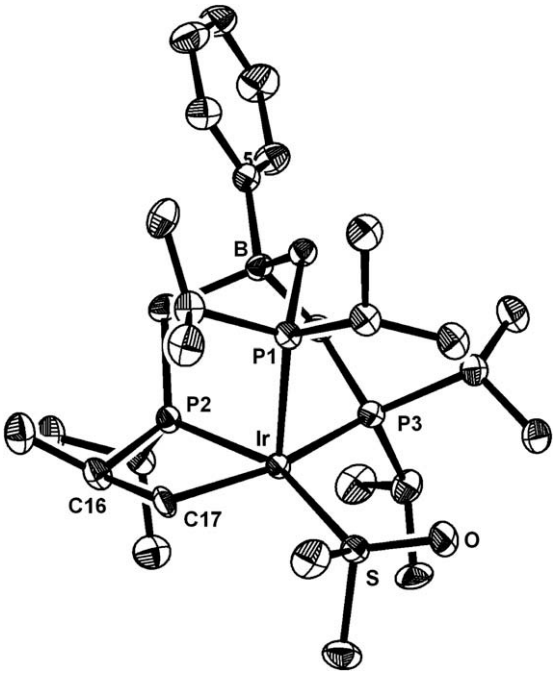

Fig. 2. DIAMOND plot of **1a** as derived by single-crystal X-ray diffraction with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–P1 2.426(1), Ir–P2 2.281(1), Ir–P3 2.390(1), Ir–C17 2.168(4), Ir–S 2.306(1); P1–Ir–P2 91.12(4), P1–Ir–P3 89.55(4), P2–Ir–P3 90.85(4), P1–Ir–C17 94.0(1), P2–Ir–C17 69.9(1), P1–Ir–S 100.27(4), P2–Ir–S 159.41(4), P3–Ir–C17 160.5(1).

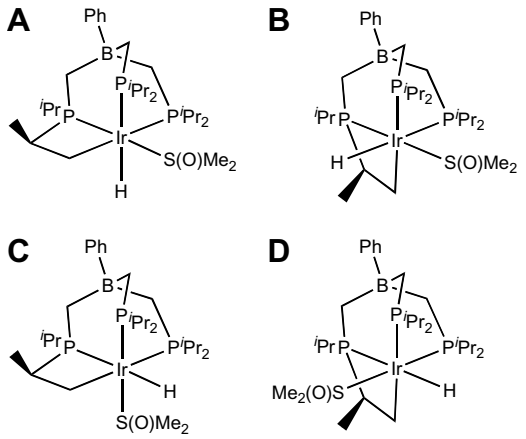

Fig. 1. Possible diastereomers of complex **1**.

Hydrogenation of a **1a**/**1b** mixture under H_2 (1 atm) in benzene affords ring opening of the four-membered metallacycle and formation of [Ir(H)$_2$(dmso){PhBP$^{iPr}_3$}] (**2**) as the only product (Scheme 1). The related complexes [Ir(H)$_2$(L){PhBP$^{iPr}_3$}] (L = PMe_3, PH_2Cy, CO) were reported earlier by Tilley and co-workers [7]. **2** features two signals in the ^{31}P NMR spectrum with a 2:1 ratio as expected

Table 1
Crystallographic data for **1a**.

	1a
Empirical formula	$C_{29}H_{59}BIrOP_3S$
Formula weight	751.79
Color/habit	Pale yellow/fragment
Crystal dimensions (mm^3)	$0.10 \times 0.18 \times 0.48$
Crystal system	Monoclinic
Space Group	$P2_1/n$ (no. 14)
a (Å)	10.1048(2)
b (Å)	17.1257(5)
c (Å)	19.0007(6)
β (°)	99.165(3)
V (Å^3)	3246.13(16)
Z	4
T (K)	153
D_{Calc} (g cm^{-3})	1.538
μ (mm^{-1})	4.346
$F(000)$	1536
θ Range (°)	2.98–25.37
Reflections collected	59342
Independent reflections/R_{int}	5917/0.043
Observed reflections ($I > 2\sigma(I)$)	4598
Data/restraints/parameters	5917/0/338
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0325/0.0876
R_1/wR_2 (all data)[a]	0.0450/0.0940
GOF (on F^2)[a]	1.074
Largest difference peak and hole (e Å^{-3})	+2.43/−1.98

[a] $R_1 = S(||F_o|-|F_c||)/S|F_o|$; $wR_2 = \{S[w(F_o^2-F_c^2)^2]/S[w(F_o^2)^2]\}^{1/2}$; $GOF = \{S[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$.

for a C_s symmetric complex. The two hydride ligands were found by ^{1}H NMR spectroscopy at −12.55 ppm as a multiplet owing to the complex AA'MXX' spin system. Heating of **1a**/**1b** at 80 °C in C_6D_6 over 4 days results in minor decomposition products (<5% by ^{31}P NMR) which could not be further characterized. However, heating of a mixture that was enriched in one of the two diastereomers did not result in equilibration of the **1a**: **1b** ratio, suggesting that the cyclometalation is irreversible under these conditions. Furthermore, no H/D exchange of the hydride ligand or on the ^{i}Pr groups was observed by ^{2}H NMR. The same observation was made for *ortho*-metalated [Ir(H)(PMe$_3$){PhB(CH$_2$PPh$_2$)$_2$(CH$_2$PPhC$_6$H$_4$)}] [8]. Feldman et al. have suggested that the catalytic deuteration of cyclooctene (COE) by [Ir(H)$_2$(COE){PhBP$^{Ph}_3$}] in C_6D_6 proceeds via an Ir(III)/Ir(V) cycle with C_6D_6 oxidative addition after COE dissociation [8]. It is reasonable to assume that dmso and PMe$_3$ are bound to Ir(III) considerably stronger than COE inhibiting benzene C–H oxidative addition. However, steric considerations have to be taken into account, as well.

3. Conclusions

The reaction of [IrCl(dmso)$_3$] with Li(THF){PhBP$^{iPr}_3$} affords two diastereomers of cyclometalated complex **1** in approximately equimolar ratio. Diastereomers with the hydride ligand in *trans* position to the metalated phosphine atom are not observed. While the facile reaction with H_2 at room temperature gives dihydride **2** quantitatively, ring opening via hydrocarbon addition was not observed rendering this system unsuitable for intermolecular aromatic C–H activation.

4. Experimental

4.1. Materials and methods

All experiments were carried out under an atmosphere of argon using Schlenk and glove-box techniques. Benzene was dried over Na/benzophenone/tetraglyme, distilled under argon, and deoxygenated prior to use. Deuterated benzene was dried by distillation from Na/K alloy. Li(THF){PhB(CH$_2$P^{i}Pr$_2$)$_3$} and [IrCl(dmso)$_3$] were prepared as reported in the literature [6b,16].

4.2. Analytical methods

Elemental analyses were obtained from the Microanalytical Laboratory of Technische Universität München. NMR spectra were recorded on a Jeol Lambda 400 spectrometer at room temperature and were calibrated to the residual proton resonance and the natural abundance ^{13}C resonance of the solvent (C_6D_6, δ_H = 7.16 and δ_C = 128.06 ppm). ^{31}P NMR chemical shifts are reported relative to external phosphoric acid (δ0.0 ppm).

4.3. Syntheses

*[Ir(H)(dmso){PhB(CH$_2$P^{i}Pr$_2$)$_2$(CH$_2$P^{i}PrCHMeCH$_2$}] (**1**).* A solid mixture of IrCl(dmso)$_3$ (0.108 g; 0.23 mmol) and [Li(THF)PhB(CH$_2$P^{i}Pr$_2$)$_3$] (0.130 g; 0.23 mmol) is dissolved in benzene (5 mL) and stirred over night. The orange-yellow solution is evaporated to dryness and the yellow-brown residue is extracted with benzene. After filtration the solvent is removed *i. vac.* to give a pale yellow microcrystalline solid consisting of a mixture of the two diastereomers **1a** and **1b** (57:43). Yield: 0.127 g (0.319 mmol; 82%). Anal. Calc. for $C_{29}H_{59}BIrOP_3S$ (751.79): C, 46.33; H, 7.91; S, 4.27. Found: C 47.18; H, 7.76; S, 3.58%.

NMR (C_6D_6, r.t., [ppm]) data for diastereomer **1a**: ^{1}H NMR (399.8 MHz): δ-11.54 (dt, 1 H, $^2J_{HP}$ = 121.5 Hz, $^2J_{HP}$ = 12.8 Hz, Ir-*H*), 0.27 (br, 1H, BC*H*$_2$P), 0.42 (br, 1H, BC*H*$_2$P), 0.52 (br, 1H, BC*H*$_2$P), 0.69 (br, 3H, BC*H*$_2$P), 0.80–1.60 (m, 36H, 11 × C*H*$_3$ + IrC*H*$_2$ + PC*H*), 1.66 (dhept, 1H, $^2J_{HP}$ = 6.8 Hz, $^3J_{HH}$ = 7.2 Hz, PC*H*), 1.94 (br, 1H, PC*H*), 2.45 (dhept, 1H, $^2J_{HP}$ = 6.7 Hz, $^3J_{HH}$ = 7.3 Hz, PC*H*), 2.53 (dhept, 1 H, $^2J_{HP}$ = 4.1 Hz, $^3J_{HH}$ = 11.3 Hz, PC*H*), 3.09 (br, 1H, PC*H*), 2.58 (s, 3H, SC*H*$_3$), 3.17 (s, 3H, SC*H*$_3$), 7.33 (t, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{para}$), 7.58 (t, 2H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{meta}$), 7.93 (d, 2H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{ortho}$). ^{31}P-{^{1}H} NMR (161.8 MHz): δ-6.9 (dd, $^2J_{PP}$ = 19.9 Hz, $^2J_{PP}$ = 14.4 Hz, *P*^{i}Pr$_2$), −10.3 (br, *P*^{i}Pr$_2$), −42.5 (t, $^2J_{PP}$ = 14.4 Hz, *P*^{i}PrCHMeCH$_2$). ^{11}B NMR (128.3 MHz): δ-12.6 (s).

NMR (C_6D_6, r.t., [ppm]) data for diastereomer **1b**: ^{1}H NMR (399.8 MHz): δ-11.96 (dt, 1H, $^2J_{HP}$ = 119.9 Hz, $^2J_{HP}$ = 11.6 Hz, Ir-*H*), 0.52 (m, 2H, BC*H*$_2$P), 0.72 (m, 4H, BC*H*$_2$P), 0.80–1.80 (m, 37H, 11 × C*H*$_3$ + IrC*H*$_2$ + 2 × PC*H*),1.87 (br, 1H, PC*H*), 2.17 (dhept, 1H, $^2J_{HP}$ = 7.3 Hz, $^3J_{HH}$ = 6.7 Hz, PC*H*), 2.30 (m, 1H, PC*H*), 2.75 (br, 1H, PC*H*), 2.78 (s, 3H, SC*H*$_3$), 2.93 (br, 1H, PC*H*), 3.11 (s, 3H, SC*H*$_3$), 7.33 (t, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{para}$), 7.58 (t, 2H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{meta}$), 7.91 (d, 2H, $^3J_{HH}$ = 7.2 Hz, C*H*$_{ortho}$). ^{31}P-{^{1}H} NMR (161.8 MHz): δ-1.3 (dd, $^2J_{PP}$ = 17.8 Hz, $^2J_{PP}$ = 13.0 Hz, *P*^{i}Pr$_2$), −12.7 (br, *P*^{i}Pr$_2$), −31.0 (t, $^2J_{PP}$ = 13 Hz, *P*^{i}PrCHMeCH$_2$). ^{11}B NMR (128.3 MHz): δ-12.1 (s).

*[Ir(H)$_2$(dmso){PhB(CH$_2$P^{i}Pr$_2$)$_3$}] (**2**).* 10 mg (13 μmol) of a mixture of **1a**/**1b** are dissolved in 0.5 mL C_6D_6 in a *J-Young* NMR tube. The solution is frozen, evacuated and backfilled with H_2 (1 atm). Over the course of 10 h **1a**/**1b** is slowly converted to [Ir(H)$_2$(dmso){PhB(CH$_2$P^{i}Pr$_2$)$_3$}] (**2**). NMR (C_6D_6, r.t., [ppm]) data of **2**: ^{1}H NMR (399.8 MHz): δ-12.55 (m, 2H, Ir-*H*), 0.80–1.60 (m, 42H, C*H*$_3$ + BC*H*$_2$), 1.67 (m, 2H, PC*H*), 1.76 (m, 2H, PC*H*), 2.74 (m, 2H, PC*H*), 3.22 (s, 6H, SC*H*$_3$), 7.33 (t, 1H, $^3J_{HH}$ = 7.0 Hz, C*H*$_{para}$), 7.59 (t, 2H, $^3J_{HH}$ = 7.3 Hz, C*H*$_{meta}$), 8.0 (br, 2H, C*H*$_{ortho}$). ^{31}P-{^{1}H} NMR (161.8 MHz): δ-15.9 (t, 1P, $^2J_{PP}$ = 17.8 Hz, *P*^{i}Pr$_2$ *trans* to dmso), −1.0 (br, 2P, *P*^{i}Pr$_2$ *trans* to H). ^{11}B NMR (128.3 MHz): δ-12.7 (s).

4.4. X-ray crystal structure determination

A clear pale yellow crystal was mounted on a glass fiber. X-ray data were collected on an Oxford Xcalibur system, using Mo Kα radiation. Data was processed and corrected for Lorentz and polarization effects, and for absorption with the Crysalis suite of programs [17]. Structural solution and refinement were carried

out with the WinGX program system [18–21]. The structure was solved by direct methods and subsequent difference Fourier syntheses. Hydrogen atoms were placed in calculated positions. Crystal and refinement data are summarized in Table 1.

Acknowledgments

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