PC(sp³)P pincer carbonyl complexes of iridium(1), and iridium(III)†

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The previously reported complex trans-[IrHCl{(cis-1,3-bis-(di-tert-butylphosphino)methyl)cyclohexane}] (2) forms the 18-electron carbonyl compound anti-[Ir(CO)HCl{(cis-1,3-bis-(di-tert-butylphosphino)methyl)cyclohexane}] (5a) upon reaction with 1 atm CO. The structural isomer syn-[IrH(CO)Cl{(cis-1,3-bis-(di-tert-butylphosphino)methyl)cyclohexane}] (5b) is obtained directly upon complexation of the ligand (1) with IrCl₂-H₂O in refluxing DMF. syn-5b is the first iridium aliphatic pincer complex with this orientation of the hydrogens and is the thermodynamically more stable isomer. Both compounds 5a and 5b afford the Ir(1) complex trans-[Ir(CO)Cl{(cis-1,3-bis-(di-tert-butylphosphino)methyl)cyclohexane}] (4) upon treatment with KOtBu. Complex 4 was also synthesised in a more straightforward fashion from the previously known terminal nitrogen complex trans-[Ir(N₂)Cl{(cis-1,3-bis-(di-tert-butylphosphino)-methyl)cyclohexane}] (3) under atmospheric CO. The complexes 4, 5a and 5b were characterised spectroscopically and in the solid state. IR data point to a more electron rich metal centre as compared to the corresponding aromatic complexes.

Experimental section

General comments

All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except where noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The ligand cis-1,3-bis-((di-tert-butylphosphino)methyl)cyclohexane, 1, and the complexes 2 and 3 were prepared according to previously reported procedures, cf. Scheme 1 for numbering. All other chemicals were purchased from commercial suppliers and used as received.

1H-, 13C and 31P-NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 (1H), 125.68 (13C) and 202.31 (31P) MHz. For 1H- and 13C-NMR spectra, the residual solvent peak was used as an internal reference. 31P-NMR spectra were referenced externally using 85% H₃PO₄ at 0 ppm. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad, (v) virtual. IR spectra were obtained on a Bruker ALPHA FT-IR spectrometer. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.
Crystallography

XRD-quality crystals of compounds 4, 5a and 5b were obtained through recrystallization from toluene or hexane. Intensity data were collected with an Oxford Diffractions Xcalibur 3 system, using ω-scans and MoKα (λ = 0.71073 A) radiation.28 The data were extracted and integrated using Crystals.29 The structure was solved by direct methods and refined by full-matrix least-squares on F2 using SHELXTL5.29

Preparation of trans-[Ir(CO)Cl(cis-1,3-bis-[(di-tert-butylphosphino)methyl]-cyclohexane) (4)]. Compound 3 (10.0 mg, 0.016 mmol) was dissolved in toluene (3 mL), and the solution was freeze–pump–thawed prior to addition of CO (1 atm). After stirring at room temperature for 1.5 h, the solvent was removed in vacuo, and the yellow solid residue was recrystallized from hexane. Yield: 7.8 mg (78%).1H-NMR (C6D6): δ 8.59 (dt, 1H, JHH = 17.0 Hz, Ir–H, 1H), 1.52 (tt, 1H, JH–Ir = 10.5 Hz, HC–Ir, 1H), 1.51–1.45 (br m, CH2–Ir, 2H + Cy, 1H), 1.41 (vt, JFe–Ir = 13.0 Hz, 1Bu, 18H), 1.37 (vt, JFe–Ir = 13.0 Hz, 1Bu, 18H), 1.12 (vt, J = 3.5 Hz, J = 14.0 Hz, Cy, 2H), 0.90 (dq, J = 4.0 Hz, J = 13.0 Hz, Cy, 2H), −8.59 (dt, JFe–Ir = 1.5 Hz, JFe–Ir = 17.0 Hz, Ir–H, 1H). 13C{1H}-NMR (C6D6): δ 192.0 (s, CH2–Ir), 191.7 (s, CH2–Ir), 126.2 (s, CH2–Ir), 117.3 (s, CH2–Ir), 114.9 (s, CH2–Ir), 111.9 (s, CH2–Ir), 109.5 (s, CH2–Ir), 109.4 (s, CH2–Ir), 105.2 (s). IR (ATR) νCO = 1977 cm−1. Anal. calcd for C22H27ClIrO2P (657.29): C, 62.58; H, 5.57. Found: C, 62.40; H, 5.38.

Preparation of syn-[IrH(Cl)Ir(CO)Cl(cis-1,3-bis-[(di-tert-butylphosphino)methyl]-cyclohexane) (5b)]. cis-1,3-Bis-[(di-tert-butylphosphino)methyl]cyclohexane (1) (24.8 mg, 0.062 mmol) and IrCl3·H2O (18.6 mg, 0.062 mmol) was mixed with dry degassed DMF (4 mL) under a stream of N2. The mixture was heated to 150 °C for 24 h. Upon cooling to RT a yellow precipitate came out of solution. The solvent was removed in vacuo, followed by repeated crystallisation from THF to afford 5b as a pale yellow crystalline powder. Yield: 23.2 mg (54%).1H-NMR (C6D6): δ 2.61–2.52 (m, CH3CH2, 2H), 2.02–1.98 (br m, Cy, 1H), 1.73–1.64 (m, Cy, 2H), 1.52 (vt, J = 4.0 Hz, J = 13.5 Hz, PCH2CH2, 2H), 1.48–1.42 (m, Cy, 1H), 1.32 (vt, J = 13.0 Hz, 1Bu, 18H), 1.26 (vt, J = 13.0 Hz, 1Bu, 18H), 1.19 (vt, J = 11.0, HC–Ir, 1H), 0.95 (dq, J = 3.5 Hz, J = 12.5 Hz, Cy, 2H). 13C{1H}-NMR (C6D6): δ 194.8 (vt, JFe–Ir = 15 Hz, Ir–CO, 1C), 71.6 (vt, JFe–Ir = 7.2 Hz, HC–Ir, 1C), 50.3 (vt, JFe–Ir = 19 Hz, PCH2CH2, 2C), 36.9 (vt, JFe–Ir = 25 Hz, Cy, 2C), 36.4 (vt, JFe–Ir = 21 Hz, CH2CH2, 2C), 35.8 (vt, JFe–Ir = 22 Hz, CH2CH2, 2C), 34.9 (vt, JFe–Ir = 19 Hz, Cy, 2C), 29.8 (vt, JFe–Ir = 5.6 Hz, CH2CH2, 6C), 29.7 (vt, JFe–Ir = 5.2 Hz, CH2CH2, 6C), 27.7 (vt, JFe–Ir = 2.8 Hz, CH2CH2, 1C). 31P{1H}-NMR (C6D6): δ 81.8 (s). IR (NaCl/nujol) νCO = 1917 cm−1, (hexane) νCO = 1920 cm−1, (CH2Cl2) νCO = 1896 cm−1.

Results and discussion

We have earlier reported on the cyclometallation of ligand 1 with [Ir(CO)Cl], to give trans-[IrH(Cl)Ir(CO)Cl] (2), and also on the reduction of this compound with metallic potassium under an N2 atmosphere at elevated temperatures, affording the Ir(i) terminal nitrogen complex 3.26 We here report an alternative synthesis of 3 from 2 under slightly milder conditions and in comparable yields, using KO’Bu (Scheme 1) as was previously reported by Milstein and Frech for the preparation of a naphthyl based PCP Rh(i) 1-N2 complex.27 Upon addition of CO to a degassed toluene solution of 3, a colour change from orange to yellow was observed within minutes, consistent with what is expected upon substitution to a stronger π–acceptor ligand. Following this route, the Ir(i) carbonyl complex 4 was isolated and characterised by IR and NMR spectroscopy and the structure was confirmed by means of X-ray crystallography. It shows a characteristic carbonyl shift at 194.8 ppm in the 13C-NMR.
spectrum. Complex 4 failed to give satisfactory elemental analysis, possibly due to a limited stability at room temperature similarly to what was found for complex 3. However, based on NMR spectra (see ESI†) it is essentially pure. The molecular structure of compound 4 is shown in Fig. 1, and the crystallographic data for the compounds 4–5 are given in Table 1. The structure adopts a distorted square planar geometry around iridium. While the angle between the PCI2 coordinated carbon and the carbonyl ligand is close to ideal (177.1°), the P–Ir–P angle is much more distorted (164.46°) due to the usual geometric constraints imposed by the chelating pincher arms. With respect to bond lengths and angles around iridium, complex 4 resembles its aromatic analogue very closely,7 and, surprisingly, there is no substantial change of the Ir– CO or C–O distances (PC2P mean distances: Ir–CO = 1.863 Å; C–O = 1.147 Å; 4: Ir–CO = 1.860(7) Å; C–O = 1.143(7)); a similar observation was made regarding the Ir(II)–N2 complexes where the aliphatic ligand was also observed to induce a small decrease in the N–N bond distance.26 However, both the N2 and current CO ligands are subject to substantial libration,23 an explanation that is unambiguous in the N2 case since the complex actually showed a shorter distance than in free N2. Therefore, a better measure of the electron density is the rCO stretching frequency. In hydrocarbons this is 1920 cm–1 for 4 compared with 1928 cm–1 for the corresponding aromatic compound.24 In dichloromethane the corresponding values are 1896 and 1913 cm–1, respectively,25 and overall this points to a more electron rich metal centre in 4 compared to the aromatic analogue, a trend that agrees with the observations of rCO stretching frequencies for Ir(II)–N2 complexes and CV-measurements for Ni(II) complexes.26

Subjecting the deep red solution of complex 2 to 1 atm CO resulted in a colourless solution of the 18 electron complex 5 within seconds. Treating a C6H6 solution of 5a with an excess of KOtBu afforded reduction to the iridium(n) complex 4, as confirmed by comparison with the NMR-spectrum of the isolated compound. The lower route is, however, slower and slightly less clean than the synthesis starting from compound 3 (Scheme 1).

Refluxing ligand 1 and IrCl3·H2O in DMF gave a yellow solid material that was shown to be complex 5b, an isomer of 5a (Scheme 2). This type of cyclometallation where the solvent is the carbonyl source, was previously observed by Azerraf and Gelman in the formation of a dibenzobarrelene based PC(sp3)3P iridium complex.27

The structural isomers 5a and 5b are clearly distinguishable by means of NMR-spectroscopy, most notably in the 31p-NMR

| Table 1 | Crystallographic data for compounds 4–5 |
|---|---|---|
| Formula | C23H20IrOP2 | C23H18IrCO2P2 | C23H16ClIrOP2 |
| Fw | 619.78 | 656.24 | 665.24 |
| Space group | Pbc/a | P21/n | Pbc/a |
| a/A | 12.4581(9) | 12.5453(2) | 12.3770(2) |
| b/A | 15.3030(9) | 15.2101(3) | 15.3452(2) |
| c/A | 29.2263(16) | 15.5649(3) | 28.8663(4) |
| β/deg | 90 | 93.996(2) | 90 |
| V/A3 | 5571.9 | 2962.80 | 5482.51 |
| Z | 8 | 4 | 8 |
| Dcalc/g cm–3 | 1.478 | 1.469 | 1.590 |
| µ/mm–1 | 4.920 | 4.718 | 5.100 |
| Refins collected | 90 480 | 70 507 | 39 527 |
| Unique refins | 6596 | 7422 | 9768 |
| R(P) (I > 2σ(I)*) | 0.0520 | 0.0332 | 0.0389 |
| wR2/F2 (all) | 0.1167 | 0.1030 | 0.1221 |
| S | 1.224 | 1.425 | 1.124 |
| Rint | 0.126 | 0.0594 | 0.0317 |
| CDDC | 1029323 | 1029333 | 1029332 |

* R = Σ|Fobs| – |Fcalc|/Σ|Fcalc|, wR2 = Σ[w(|Fobs| – |Fcalc|)2]/Σ(|Fcalc|2), S = Σ[w(|Fobs| – |Fcalc|)2]/Σ(|Fcalc|2)1/2.

Fig. 1 Molecular structure of 4 at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.143(6), Ir1–C9 = 1.860(7), C9–O1 = 1.143(7), Ir1–P1 = 2.3073(16), Ir1–P2 = 2.3060(15), P1–Ir1–P2 = 164.46(6), C1–Ir–C9 = 177.1(3), C1–Ir–C9–O1 = 179.1(7), P1–Ir1–C1 = 82.38(16), P2–Ir1–C1 = 82.14(16).

Fig. 2 Molecular structure of 5a and 5b at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: 5a: Ir1–C1 = 2.137(4), Ir1–C9 = 1.943(4), C9–O1 = 1.101(5), Ir1–C1 = 2.5374(10), Ir1–P1 = 2.3591(10), Ir1–P2 = 2.3643(10), P1–Ir1–P2 = 158.44(4), C1–Ir–C9 = 87.16(16), Ir1–C9–O1 = 173.7(4), C1–Ir1–C1 = 179.40(11), P1–Ir1–C1 = 95.53(4), P2–Ir1–C1 = 96.39(4), 5b: Ir1–C1 = 2.159(4), Ir1–C9 = 1.909(5), C9–O1 = 1.111(6), Ir1–C1 = 2.5340(12), Ir1–P1 = 2.3578(11), Ir1–P2 = 2.3555(11), P1–Ir1–P2 = 161.82(4), C1–Ir–C9 = 174.72(18), Ir1–C9–O1 = 174.14(4), C1–Ir1–C1 = 90.49(12), P1–Ir1–C1 = 94.15(4), P2–Ir1–C1 = 94.44(4).
shifts (δ = 50.2 ppm and 56.4 ppm respectively in C_6D_6) and the ^1H-NMR hydride shifts (δ = −8.59 ppm and −18.7 ppm respectively in C_6D_6), and both compounds are seemingly resistant towards isomerisation upon standing in solution at room temperature for several days. A significantly lower solubility of compound 5b made attempts to obtain a satisfactory ^13C-NMR spectrum of this compound unsuccessful. However, crystallographic and IR spectroscopic data clearly confirm the presence of a carbonyl ligand. The ν_{CO} stretching frequencies for 5a and 5b are found at 1977 cm⁻¹ and 1989 cm⁻¹ respectively, which can be compared to the value reported for the aromatic analogue of 5a (ν_{CO} = 1985 cm⁻¹, KBr).^{15} Thus, it is again clear that the electron density at iridium bonded to a C(sp³)-carbon is higher than in an analogous aromatic complex. Also, the π-back donation is weaker trans to a σ-bonded carbon than trans to the hydride ligand. As expected the ν_{CO} values in the Ir(III) complexes 5a and 5b are substantially higher than the value in the Ir(I) complex 4.

The molecular structures of compound 5a and 5b are given in Fig. 2. Notably, the two isomers 5a and 5b have different orientations of their respective hydride ligands relative to the α-hydrogen, as illustrated in Schemes 1 and 2. In case of 5a, the hydride and α-hydrogen are located anti to each other, while in 5b they are syn. All previously reported PC(sp³)P complexes with iridium show an anti configuration and this seems to be the preferred outcome of a metallation involving a concerted oxidative addition process via a C–H σ-complex. This is therefore what is observed in the fast CO addition to 2 which has an anti configuration. Gelman observed that the quality of the DMF influenced the outcome of the cyclometallation reaction, affording a PC(sp³)PIrH(CO)Cl complex in the presence of water and a PC(sp³)PIr(CO)(Cl)₂ complex in dry solvent, but 5b is analogous to the complex reported in wet DMF, featuring the carbonyl ligand located in a trans position and the hydride and chloride both in cis position to the metallated PCP carbon, although DMF freshly distilled from CaH₂ was used.

The observations by Gelman and the syn configuration of the hydride ligand and α-hydrogen in 5b probably means that the mechanism for formation of the cyclometallated species in DMF is not a simple C–H oxidative addition but involves several deprotonation/protonation steps. There was no tendency for isomerization of 5b. Overall, this indicates that the syn configuration is thermodynamically more stable than the anti one and this is also in line with the higher density for 5b. To test this hypothesis, we attempted isomerisation of 5a to 5b (Scheme 3). Indeed, when a solution of 5a in C_6D_6 was heated at 90 °C, signals of 5b appeared, together with very small amounts of 4 and another compound, which is characterized by a doublet at 57.6 ppm in the ^31P(^1H) NMR spectrum and a triplet at −18.78 (J_{PH} = 11.8 Hz) in the ^1H NMR spectrum. Based on the similarity of the NMR signals of this new compound and those of 5b, we tentatively ascribe it to the structure 5c, i.e. the anti isomer with CO trans to the σ-C bond. After 36 h the reaction was complete and only 5b together with traces of 4 was observed. These observations suggest that most likely the isomerisation of 5a to 5b proceeds via a reversible dehydrochlorination to give 4, followed by protonation syn (to give 5b) or anti (to give 5c) with respect to the α-CH of 4.

DFT calculations confirm the relative thermodynamic stability of 5a, 5b and 5c. Thus, energies of 5a and 5c are almost equal, while complex 5b is 7.4 kcal lower than 5a and 5c in agreement with experimental observations (see ESI† for details).

Conclusions

In summary, we have described the synthesis of new cyclohexyl-based PCP carbonyl complexes with iridium(I) and iridium(III). As noted earlier, the C(sp³) ligand gives a more electron rich metal complex than observed for the corresponding aromatic systems. Furthermore, we have, for the first time, isolated the thermodynamically more stable syn isomer of a PC(sp³)P complex with iridium.

Acknowledgements

Financial support from the Swedish Research Council, the Knut and Alice Wallenberg Foundation and the Royal Physiographic Society in Lund is gratefully acknowledged.
References


18 B. Rybtchinski, Y. BenDavid and D. Milstein, Organometallics, 1997, 16, 3786.
31 CrystalMaker® Software, Begbroke Science Park, Sandy Lane, Yarnton, Oxfordshire, OX5 1PF, United Kingdom, 2010.