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Cyclometalation of Phosphanes at Iridium(I): Interplay with Intramolecular Reductive Elimination Induced by the Strong π -Acceptor Ligands CO and NO⁺

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

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Reaction of [{Ir(μ -Cl)(coe)_2]2] (1; coe = *cis*-cyclooctene) with 4 equiv. of $PtBu_2Ph$ in CH₂Cl₂ at ambient temperature resulted in oxidative addition of one phosphane ligand affording the known cyclometalated Ir^{III} complex [IrCl(H)-($PtBu_2C_6H_4$ - κ^2P ,C)($PtBu_2Ph$)] (2) in high yield. Compound 2 exhibits a coordinatively unsaturated five-coordinate 16 VE species, and its reactivity towards strong π -acceptor ligands is investigated. Reaction of 2 with CO resulted in addition of

Introduction

Some years ago we reported the synthesis and X-ray crystal structure of olefinic complex trans-[IrCl(coe)- $(PtBu_2H)_2$ (coe = *cis*-cyclooctene), which was obtained by treating $[{Ir(\mu-Cl)(coe)_2}_2]$ (1) with secondary phosphane PtBu₂H in CH₂Cl₂ at room temperature using a molar ratio of Ir/P = 1:1.5.^[1] These defined conditions should be warranted since, by the use of a molar ratio of 1 Ir/P =1:2, the formation of $[IrCl(PtBu_2H)_3]^{[2]}$ is observed to some extent. Since only a few molecular structure determinations on trans-[IrCl(coe)(phosphane)₂] complexes had been reported, we were interested in examining the analogous reaction of 1 with tertiary phosphane PtBu₂Ph. However, our investigations in this field resulted, unexpectedly, in facile cyclometalation including the ortho position of the phenyl group in one phosphane ligand affording the cyclometalated, coordinatively unsaturated complex [IrCl(H)- $(PtBu_2C_6H_4-\kappa^2 P,C)(PtBu_2Ph)$] (2).^[3] Initially, we assumed that the formation of a stable Ir-C bond was the driving force in this reaction. Contrary to this finding, we observed in reactions of 1 with strong π -acceptor ligands such as CO and NO⁺ a spontaneous inversion of cyclometalation at room temperature resulting in reductive elimination from

 [a] Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstraße 5-13, 81377 München E-mail: hans.boettcher@cup.uni-muenchen.de http://www.cup.uni-muenchen.de the CO ligand and inversion of cyclometalation to give known Ir^{I} complex *trans*- $[IrCl(CO)(PtBu_{2}Ph)_{2}]$ (3). In a similar manner, 1 reacted with nitrosonium tetrafluoridoborate affording the new complex salt $[IrCl(NO)(PtBu_{2}Ph)_{2}][BF_{4}]$ (4), which is isoelectronic with 3. Compounds 2 and 4 were characterized by spectroscopic methods as well as by X-ray crystallography confirming their molecular structures.

compound **2** to generate the corresponding iridium(I) complexes. This reaction was presumably induced by coordination of the strong π -acceptor ligand. In light of this finding, we report herein the full characterization of compound **2** including its molecular structure by X-ray crystallography along with selected studies on the reactivity of this coordinatively unsaturated species towards several ligands.

Results and Discussion

Treatment of 1 with $PtBu_2Ph$ (molar ratio of Ir/P = 1:1.5and 1:2) in CH_2Cl_2 at room temperature resulted, in the early stage of the reaction, in a red-brown suspension that changed into a clear deep-red solution within 15 min. We cannot exclude that, in this period, the expected complex trans-[IrCl(coe)(PtBu₂Ph)₂] was present in the reaction mixture. However, NMR investigations after a very short reaction time showed that compound 2 was quickly formed as the sole product. After 1 h, $[IrCl(H)(PtBu_2C_6H_4 \kappa^2 P, C$)(PtBu₂Ph)] (2)^[3] was isolated from the reaction mixture as dark red crystals in good yield. Notably, treatment of 1 with $PtBu_2Ph$ in a molar ratio of Ir/P = 1:3 using analogous conditions resulted also exclusively in the formation of compound 2. Coordinatively saturated iridium(III) complexes often exhibit a yellow color. In contrast to this observation, complex 2 was intensely red-brown. This can be presumably attributed to low-energy, metal-based elec-



tronic transitions in the HOMO-LUMO region; the intense color was a first hint at the coordinatively unsaturated character of this species. Corresponding UV/Vis absorption bands were observed in a pentane solution of 2 (see Exp. Sect.). Indeed, the hypothesized coordinative unsaturation was ultimately confirmed by X-ray crystallographic data generated using single crystals of 2 (see below). In the literature it is well established that (phosphane)iridium(I) complexes bearing suitable substituents on the phosphorus atom (e.g. phenyl groups) can undergo facile intramolecular oxidative addition reactions under mild conditions affording products that contain cyclometalated phosphane ligands.^[4] Complex 2 was characterized by elemental analysis, NMR spectroscopy (1H, 31P and 13C) and mass spectrometry. Our findings corresponded well with the reported data,^[3] and we were able to collect more data in detail (see Exp. Sect.). Correspondingly, we found better resolved signals in the ¹H NMR spectrum in the region of aromatic protons. Some broad resonances, centered at $\delta = 7.88$ and 7.37 ppm, can be attributed to phosphane interconversions by reversible metalation/demetalation of the ortho-hydrogen atoms on the two different phosphane ligands as discussed in the literature.^[5] The ${}^{31}P{}^{1}H$ NMR spectrum of 2 in CD₂Cl₂ at room temperature consists of a pattern corresponding to an AX (almost AB) spin system. A trans arrangement of both phosphorus-containing ligands is clearly indicated by the large coupling constant ${}^{2}J_{PP} = 335.1$ Hz. The chemical shift of one signal in the high-field region at $\delta = -11.2$ ppm was an indication that the expected complex with the constitution trans-[IrCl(coe)(PtBu₂Ph)₂] was not obtained. Such a large shift to upfield values was indicative of an ortho-metalation process.^[6] The ¹H NMR spectrum confirmed unambiguously the presence of a phosphane beside a cyclometalated phosphane and a hydrido ligand in the product. Finally, the molecular structure of 2 was corroborated by an X-ray diffraction study confirming that $[IrCl(H)(PtBu_2C_6H_4-\kappa^2P,C)(PtBu_2Ph)]$ (2) was the sole product of this reaction. In the literature^[3] it has been argued that compound 2 is an intermediate in the synthesis of complex $[Ir(H)_2Cl(PtBu_2Ph)_2]$ from $[{Ir(\mu-Cl)(coe)_2}_2]$ and PtBu₂Ph, and that an Ir^I center in products derived from the reaction of $[{Ir(\mu-Cl)(olefin)_2}_2]$ with phosphane has an exceptional ability to metalate C-H bonds. Our data support the correctness of this statement, although the phosphane ligands should be amenable to cyclometalation. In the case of secondary phosphane $PtBu_2H$ – as a comparative starting point of our investigations - this was not possible.

Compound 2 crystallized from toluene/ethanol at -30 °C as red block-like crystals belonging to the monoclinic space group $P2_1/c$ with four molecules in the unit cell. A view of the molecular structure in the crystal is depicted in Figure 1, selected bond lengths and angles are given in the caption. The crystal-structure determination revealed a five-coordinate iridium(III) complex with distorted a square-pyramidal polyhedron shape with an apical hydrido ligand. The strong σ -donor hydrido ligand is arranged *trans* to the empty coordination site confirming the hypothesis of the

earlier report.^[3] Moreover, the very large chemical shift of the hydrido signal into the high-field region in the ¹H NMR spectrum was indicative of such an environment.^[5] Compound **2** exhibits a valence-electron count of 16 VE and is therefore an electronically and coordinatively unsaturated species.



Figure 1. ORTEP view of the molecular structure of **2** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ir1–P1 2.3248(9), Ir1–P2 2.3400(8), Ir1–C1 2.051(3), Ir1–Cl1 2.4118(9), Ir1–H1 1.42(5), P2–C21 1.885(3), C1–C2 1.409(4), P1–C2 1.800(3), P1–C7 1.877(3), P1–C11 1.871(3), P2–C15 1.841(3), P2–C21 1.885(3) P2–C25 1.904(3); P1–Ir1–P2 169.11(3), P1–Ir1–C1 68.38(8), Ir1–P1–C7 116.53(10), Ir1–P2–C25 116.64(9), C11–Ir1–C1 160.35(9), C1–Ir1–H1, 84.6(17), P1–Ir1–H1 85.9(17), P2–Ir1–H1, 91.3(16).

In light of the coordinative unsaturation of species 2, we examined its reactivity towards small molecules by investigating possible addition reactions. Thus, treatment of compound 2 with carbon monoxide in CH₂Cl₂ at room temperature resulted spontaneously in a reaction characterized by a color change from deep red to slightly yellow. From the solution, pale yellow crystals in high yield were isolated exhibiting a very strong v(CO) band in the IR spectrum at 1974 cm⁻¹ (solid, ATR). Surprisingly, in the ³¹P{¹H} NMR spectrum (CD₂Cl₂) at room temperature only a singlet at δ = 51.5 was observed. This latter circumstance was an indication that smooth addition of CO to compound 2 did not occur. These spectroscopic data alone suggested that the reaction product was known compound trans- $[IrCl(CO)(PtBu_2Ph)_2]$ (3)^[7] (Scheme 1). Indeed, we unambiguously confirmed the identity of this species by further analytical methods (see Exp. Sect.). Comparable reactivity has been observed in the literature only in very few cases. Caulton and co-workers reported that the coordinatively unsaturated iridium(III) complexes [Ir(H)₂X(PtBu₂Ph)₂] (X = halide or other anions) reacted quickly with CO.^[8] Subsequently, the adducts with CO were able to reductively eliminate HX, although this reaction was strongly dependent on the electronic properties of the coordinated ligand X. Interestingly, the complexes containing X = F or OPh

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quickly lost HX by spontaneous reductive elimination upon reaction with CO. On the other hand, for the complexes with X = Cl, Br, I or N₃, stable iridium(III) adducts with CO were isolated.^[8]



Scheme 1. Synthesis of *trans*- $[IrCl(CO)(PtBu_2Ph)_2]$ (3) and *trans*- $[IrCl(NO)(PtBu_2Ph)_2]BF_4$ (4).

Moreover, Caulton and co-workers reported numerous studies of coordinatively unsaturated complexes bearing bulky phosphane ligands that influence steric protection of empty coordination sites without any direct interaction with the central atom beyond metal-phosphorus bonding.^[9] However, remarkable exceptions were reported for cyclometalated phosphane complexes where intramolecular C-H activations (oxidative addition) facilitate reductive elimination processes from Ir^{III} complexes.^[9] Previously, a similar reductive elimination at an ortho-metalated hydridoiridium(III) complex containing a tripodal tetraphosphorus ligand was reported.^[10] However, in this case, a cyclometalated, coordinatively saturated IrIII species bearing a hydrido ligand underwent inversion of the cyclometalation during reaction with carbon monoxide. The reaction described needed rougher conditions (5 bar CO, 2 weeks at room temperature, 80% conversion). In contrast, the reaction of 2 with CO occurred spontaneously under normal conditions and in nearly quantitative yield. The spontaneous reaction could be attributed to the coordinative unsaturation of compound 2. We assume that, in the first step of the reaction, addition of CO to the unsaturated complex 2 occurred. Moreover, we think that steric hindrance should not deter addition of the relatively small CO molecule to 2. In light of this, we have some indications that acetonitrile, for instance, adds as the ligand to 2 resulting in the corresponding coordinatively saturated species. Unfortunately, the latter species is very labile in solution, (e.g., workup under vacuum conditions resulted in a loss of acetonitrile affording complex 2 back). Therefore, the inversion of cyclometalation in the reaction of 2 with CO is more likely attributable to the special bonding situation in the resulting product. Ir^{III} complexes are less favoured to coordinate the strong π -acceptor ligand CO than are Ir^I compounds. Therefore, we believe that the driving force in cyclometalation inversion is provided by attainment of a preferred bonding situation for the incoming CO ligand. To support this assertion we examined the reaction of compound 2 with the strong π -acceptor ligand NO⁺. Thus, treatment of equimolar amounts of compound 2 and $NO[BF_4]$ in CH₂Cl₂ at room temperature resulted, after 1 h, in a reaction with a color change from deep-red to violetbrown. From the solution, dark red crystals could be isolated in high yield. The solid exhibited a very strong v(NO)band in the IR spectrum (ATR) at 1873 cm⁻¹ clearly indicating coordination of the NO⁺ ligand in the coordination sphere. As observed for *trans*- $[IrCl(CO)(PtBu_2Ph)_2]$ (3) in the ${}^{31}P{}^{1}H$ NMR spectrum (CD₂Cl₂) at room temperature, only a singlet at δ = 52.6 ppm was observed. Therefore, also in this case, the addition of NO^+ to compound 2 occurred with reductive elimination of the cyclometalated phosphane ligand resulting in the formation of the new compound trans-[IrCl(NO)(PtBu₂Ph)₂][BF₄] (4) (Scheme 1). The identity of this species was confirmed by spectroscopic and analytical data (see Exp. Sect.), and its molecular structure was determined by X-ray diffraction analysis. Compound 4 crystallized by the diffusion method from CH₂Cl₂/ MeOH at room temperature as red block-like crystals belonging to the monoclinic space group $P2_1/c$ with four molecules in the unit cell. A view of the molecular structure of 4 in the crystal is depicted in Figure 2; selected bond lengths and angles are given in the caption. Corresponding complexes *trans*-[IrX(NO)(PPh₃)₂]⁺ (X = Cl, OH, OR) were described in the literature long ago;^[11] however, no crystalstructure reports for this type of complex have been pub-



Figure 2. ORTEP view of the molecular structure of compound **4** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ir1–Cl1 2.2652(7), Ir1–P1 2.429(6), Ir1–P2 2.429(6), Ir1–N1 1.734(19), P1–C1 1.890(2), P1–C5 1.878(3), P1–C9 1.828(2), P2–C15 1.881(2), P2–C19 1.892(3), P2–C23 1.834(2), B1–F1 1.382(3); Cl1–Ir1–P1 90.75(2), P1–Ir1–P2 178.31(2), P1–Ir1–N1 89.71(6), Ir1–P1–C1 118.50(7), Ir1–P1–C5 106.59(8), Ir1–P1–C9 105.59(7), Ir1–P2–C15 106.56(8), Ir1–P2–C19 118.57(8), Ir1–P2–C23 105.68(8), Ir1–N1–O1 178.99(18).



lished to date. The coordination sphere around the iridium atom in the cationic complex can best be described as nearly square-planar with the bulky phosphane ligands *trans*-positioned relative to each other. The nitrosyl ligand exhibiting a bond angle Ir1–N1–O1 of 178.99(18)° can be clearly identified as an NO⁺ ligand corresponding very well to the characteristic v(NO) band at 1873 cm⁻¹. The P–Ir1– P angle deviates from the ideal value of 180° only by 1.7°. Even the Cl–Ir–N angle is close to 180° indicating an approximately square-planar coordination sphere for the Ir^I cationic complex.

The cationic complex in compound 4 can be considered a close relative of the isoelectronic species *trans*- $[IrCl(CO)(PPh_3)_2]$, the well-known Vaska compound.^[12]

Currently, we are working in the field of reaction studies of 2 with other strong π -acceptor ligands and a series of other σ -donor ligands. Here we have some indications that the closely related compound *trans*-[IrCl(PF₃)(PtBu₂Ph)₂] can be obtained in a fashion similar to that used to access compounds 3 and 4. Unfortunately, the complex bearing the PF₃ ligand is very unstable at room temperature in solution – a circumstance that renders more difficult its characterization by NMR spectroscopic methods. Nevertheless, we obtained preliminary X-ray crystal-structure results confirming the molecular structure of this species. Furthermore, we examined the reactivity of 2 towards the ligands PMe_3 , PPh_3 and $P(OPh)_3$. These reactions were not easy to investigate as indicated by the formation of mixtures of products, which are strongly influenced by the chosen molar ratios between iridium and the incoming ligand. The reaction solutions obtained were difficult to handle at room temperature; transformations were often revealed using NMR methods. Continued investigations in this field are in progress in our laboratory. However, these studies are challenging by virtue of the fact that, at room temperature, facile metalation and demetalation processes must be carefully controlled.

Conclusions

We have investigated the reaction of $[{Ir(\mu-Cl)(coe)_2}_2]$ (1) with tertiary phosphane $PtBu_2Ph$ with the aim of generating trans-[IrCl(coe)(PtBu₂Ph)₂]. Instead, facile ortho metalation of one of the phenyl groups gave rise to the formation of known cyclometalated Ir^{III} complex $[IrCl(H)(PtBu_2C_6H_4-\kappa^2 P,C)(PtBu_2Ph)]$ (2). This coordinatively unsaturated species reacted smoothly with the strong π -acceptor ligands CO and NO⁺ affording iridium(I) complexes trans-[IrCl(CO)(PtBu₂Ph)₂] (3) and trans- $[IrCl(NO)(PtBu_2Ph)_2]^+$, respectively. Originally, we expected reactions upon addition of these small molecules. Instead, and quite unexpectedly, inversion of cyclometalation was observed. We attribute this reaction behavior to a better donor-acceptor situation in the resulting iridium(I) product than is the case for the corresponding iridium(III) complex. Caulton and co-workers reported that coordinatively unsaturated iridium(III) complexes [Ir(H)₂-

 $X(PtBu_2Ph)_2$] (X = F, OPh) reacted quickly with CO under reductive-elimination conditions to afford complexes [IrH(CO)₂(PtBu₂Ph)] and [IrH(CO)(PtBu₂Ph)₂], respectively.^[8,13] Since, in the case of X = Cl, for example, a stable addition product of Ir^{III} with CO, namely [Ir(H)₂Cl-(CO)(PtBu₂Ph)₂], was isolated, we have to conclude that this reaction behavior is not directly comparable to our reactions described therein. We started with a compound containing a metalated C–H bond and, as mentioned above, such a situation seemed to facilitate reductive elimination from Ir^{III} complexes.^[9,14]

Experimental Section

General: All reactions were carried out under dry nitrogen using standard Schlenk techniques. Reagents were purchased commercially from ABCR and used without further purification. [{Ir(µ- $Cl(coe)_{2}_{2}$ (1) was prepared from hydrated iridium(III) chloride and *cis*-cyclooctene according to a published procedure.^[15] IR spectra were recorded from solids with a JASCO FT/IR-460 Plus spectrometer equipped with an ATR unit. NMR spectra were obtained using Jeol Eclipse 270 and 400 instruments operating at 270 and 400 (1H), 109 MHz (31P), and 68 MHz (13C), respectively. Chemical shifts are given in ppm from SiMe₄ (¹H, ¹³C) or 85% H_3PO_4 (³¹P). Mass spectra were recorded using a Jeol MStation JMS-700 instrument. UV/Vis spectra were recorded with a Varian Cary 300 double-beam spectrometer. Microanalyses (C, H, Cl, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

 $[IrCl(H)(PtBu_2C_6H_4-\kappa^2P,C)(PtBu_2Ph)]$ (2): To a solution of 1 (448 mg, 0.50 mmol) in CH₂Cl₂ (20 mL) was added PtBu₂Ph (444 mg, 0.48 mL, 2.00 mmol) and the mixture stirred for 1 h. During an initial time of 15 min, a red-brown suspension resulted, which changed subsequently into a dark red solution. The solvent was evaporated in vacuo, and *n*-hexane (10 mL) was added to the residue affording a red-brown microcrystalline precipitate. The solid was filtered off, washed with cold pentane (3 mL), and dried in vacuo. Yield: 570 mg (85%). C₂₈H₄₆ClIrP₂ (672.29): calcd. C 50.02, H 6.90, Cl 5.27; found C 49.84, H 6.98, Cl 4.98. ³¹P{¹H} NMR (109 MHz, CD₂Cl₂, 20 °C): δ = 52.3 (d, ²J_{PP} = 335.3 Hz, *Pt*Bu₂Ph), -11.2 (d, ${}^{2}J_{PP}$ = 335.3 Hz, $PtBu_{2}C_{6}H_{4}$) ppm. ¹H NMR (400 MHz, CD_2Cl_2 , 20 °C): δ = 7.88 (br. s, 2 H), 7.37 (t, J_{HH} = 7.0 Hz, 1 H), 7.32 (br. s, 2 H), 6.84 (t, $J_{\rm HH}$ = 8.4 Hz, 1 H), 6.67 (dt, $J_{\rm HH}$ = 7.5, $J_{\rm HH}$ = 2.6 Hz, 1 H), 6.50 (dt, $J_{\rm HH}$ = 7.6, 1.0 Hz, 1 H), 5.79 (dd, $J_{\rm HH}$ = 7.8, 4.4 Hz, 1 H), 1.59 (d, ${}^{3}J_{\rm PH}$ = 13.2 Hz, 9 H, t-C₄H₉), 1.47 (d, ${}^{3}J_{PH}$ = 14.0 Hz, 9 H, *t*-C₄H₉), 1.41 (d, ${}^{3}J_{PH}$ = 14.0 Hz, 9 H, t-C₄H₉), 1.33 (d, ${}^{3}J_{PH}$ = 13.2 Hz, 9 H, t-C₄H₉), -42.1 (br. pseudo-t, ${}^{2}J_{\rm PH}$ = 11.4, ${}^{2}J_{\rm PH}$ = 11.2 Hz) ppm. ${}^{13}C{}^{1}H$ NMR (68 MHz, CD₂Cl₂, 20 °C): δ = 150.5 (d, J_{PC} = 40.3 Hz, C₆H₄), 136.9 (dd, J= 13.4, 1.9 Hz, cyclometalated C), 132.2, (d, J = 32.6 Hz, C₆H₄), 129. 5 (s), 128.3 (s, C₆H₅), 127.5 (s), 121.4 (d, ${}^{2}J_{PC} = 7.7$ Hz, C₆H₄), 37.7 (dd, ${}^{3}J_{PC} = 18.7$, 3.9 Hz, P-C-CH₃), 37.2 (dd, ${}^{3}J_{PC} = 17.3$, J_{PC} = 2.9 Hz, P-C-CH₃), 35.5 (dd, ${}^{3}J_{PC}$ = 13.9, J_{PC} = 3.8 Hz, P-C-CH₃), 33.2 (dd, ${}^{3}J_{PC}$ = 14.4, J_{PC} = 4.8 Hz, P-C-CH₃), 32.3 (d, ${}^{2}J_{PC}$ = 4.8 Hz, P-C-CH₃), 30.1 (br., P-C-CH₃), 30.0 (d, ${}^{2}J_{PC}$ = 2.9 Hz, P-C-CH₃), 29.3 (d, ${}^{2}J_{PC}$ = 1.9 Hz, P-C-CH₃) ppm. MS (DEI): m/z= 672 [M⁺], 636 [M⁺ - Cl], 580 [M⁺ - C₄H₉], 522 [M⁺ - 2 C₄H₉]. UV/Vis (pentane): λ_{max} (ε) = 312 (6962), 426 (3280), 486 $(2375 \text{ cm}^{-1} \text{ M}^{-1})$ nm. Suitable single crystals of 2 for X-ray diffraction were obtained from toluene/ethanol solution by cooling to -30 °C for 2 d.



trans-[IrCl(CO)(PtBu₂Ph)₂] (3): Compound 2 (336 mg, 0.50 mmol) was dissolved in CH₂Cl₂ (20 mL), and a slow stream of carbon monoxide was bubbled through the solution at room temperature for ca. 2 min. During this time the color of the solution changed spontaneously from deep red to nearly colorless. The mixture was stirred under the resulting CO atmosphere for 30 min. The solution was concentrated to dryness and the remaining residue crystallized from CH₂Cl₂/MeOH affording slightly yellow crystals. Yield: 345 mg (98%). C₂₉H₄₆ClIrOP₂ (700.30): calcd. C 49.74, H 6.62, Cl 5.06; found C 50.02, H 6.43, N 4.93. IR (solid): $\tilde{v} = 1974$ (vs, CO) cm⁻¹. ³¹P{¹H} NMR (109 MHz, CD₂Cl₂, 20 °C): δ = 51.5 (br. s) ppm. ¹H NMR (270 MHz, CD₂Cl₂): δ = 8.13–8.06 (m, 2 H, C₆H₅), 7.41–7.34 (m, 3 H, C_6H_5), 1.54 (pseudo-t, 18 H, PC_4H_9) ppm. ¹³C{¹H} NMR (68 MHz, CD₂Cl₂, 20 °C): δ = 171.8 (t, ²J_{PC} = 12.1 Hz, CO), 136.3 (m, C_6H_5),133.8 (t, $J_{PC} = 19.3$ Hz, C_6H_5 , C_{ipso}), 129.3 (s, C_6H_5), 126.6 (m, C_6H_5), 37.5 (t, $J_{PC} = 10.4$ Hz, CCH₃), 30.8 (s, CCH₃) ppm. MS (DEI): *m*/*z* = 700 [M⁺], 643 [M⁺ - C_4H_9], 615 [M⁺ - C_4H_9 - CO], 560 [M⁺ - Cl - CO - C_6H_5].

trans-[IrCl(NO)(PtBu₂Ph)₂][BF₄](4): Compound 2 (370 mg, 0.55 mmol) was dissolved in CH₂Cl₂ (20 mL), NO[BF₄] (75 mg, 0.64 mmol) was added and the mixture stirred at room temperature for 2 h resulting in a violet-brown solution. The solvent was evaporated in vacuo and the residue crystallized from CH₂Cl₂/Et₂O affording dark red crystals suitable for X-ray diffraction. Yield: 395 mg (91%). C₂₈H₄₆BClF₄IrNOP₂ (789.10): calcd. C 42.62, H 5.88, Cl 4.49, N 1.78; found C 42.75, H 6.05, Cl 4.23, N 1.52. IR (solid): $\tilde{v} = 1873$ (s, NO) cm⁻¹. ³¹P{¹H} NMR (109 MHz, CD₂Cl₂, 20 °C): $\delta = 52.6$ (br. s) ppm. ¹H NMR (270 MHz, CD₂Cl₂): $\delta = 7.97-7.93$ (m, C₆H₅), 7.58-7.54 (m, C₆H₅), 1.67 (pseudo-t, 18 H, PC₄H₉) ppm. ¹³C{¹H} NMR (68 MHz, CD₂Cl₂, 20 °C): $\delta = 135.7$ (m, C₆H₅), 132.2 (m, C₆H₅), 128.8 (m, C₆H₅), 126.9 (t, J = 21.4 Hz,

Table 1. Details of the X-ray crystal-data collection and structure refinement for compounds 2 and 4.

	2	4
Empirical formula	C ₂₈ H ₄₆ ClIrP ₂	C ₂₈ H ₄₆ BClF ₄ IrNOP ₂
M _r	672.282	789.093
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	15.3422(7)	14.2979(6)
b [Å]	13.9596(6)	13.7215(6)
c [Å]	14.7662(6)	16.8382(7)
β [°]	115.1450(10)	93.6298(12)
$V/Å^3$	2862.8(2)	3296.8(2)
Ζ	4	4
<i>T</i> [K]	100(2)	173(2)
$\rho_{\rm calcd.} [\rm g cm^{-3}]$	1.55982(11)	1.58983(10)
$\mu \text{ [mm^{-1}]}$	4.883	4.272
θ range for data collection [°]	3.04 to 27.51	2.97 to 27.57
Reflections collected	51303	78172
Independent reflections	6586	7618
R _{int}	0.0544	0.0357
$R_1 \left[I > 2\sigma(I) \right]$	0.0243	0.0194
wR_2 (all data)	0.0480	0.0419
Parameters	305	364
Goodness of fit on F^2	1.038	1.054
Largest difference peak/hole [eÅ-3]	1.217/-0.573	1.435/-0.499

 C_6H_5), 40.2 (t, J_{PC} = 9.9 Hz, CCH₃), 30.9 (s, CCH₃) ppm. MS (DEI): $m/z = 702 [M^+ - BF_4], 442 [M^+ - BF_4 - PtBu_2Ph - NO].$ Crystal-Structure Determination and Refinement: Crystals suitable for X-ray crystallography of 2 and 4 were obtained as described above. Crystals were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated with an OxfordXCalibur and a Bruker Nonius-Kappa CCD diffractometer, respectively, using graphite-monochromated Mo- K_a radiation (λ = 0.71073 Å). The structures were solved by Direct Methods (SIR97) ^[16] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).^[17] Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details of the crystal data, data collection, structure solution, and refinement parameters of compounds 2 and 4 are summarized in Table 1. CCDC-1053539 (for 2) and CCDC-1053540 (for 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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