Reactions of iridium bis(phosphinite) pincer complexes with protic acids

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Iridium pincer complexes [C_6H_3-2,6-($OPBu^t_2$)$_2$]Ir(H)Cl (**10**) and [4-EtOOCC_6H_2-2,6-($OPBu^t_2$)$_2$]Ir(H)Cl (**11**) react with protic acids undergoing metallation of one of the *tert*-butyl groups to form double cyclometallated products [4-R-C_6H_2-2-($OPBu^t_2$)-6-(OP(Bu^t)CMe_2CH_2)]IrCl (**12**, R = H; **13**, R = COOEt), which are stable in air. Complex **12** reacts with CO and Bu^tNC giving the corresponding 18-electron complexes [C_6H_3-2-($OPBu^t_2$)-6-(OP(Bu^t)CMe_2CH_2)]Ir(L)Cl (**14**, L = CO; **15**, L = CNBu^t). The structure of compound **14** was established by X-ray diffraction analysis.

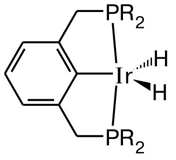
Key words: cyclometallation, iridium hydrides, pincer complexes, protic acids, X-ray diffraction analysis.

Homogeneous catalytic dehydrogenation of saturated hydrocarbons is one of the most important problems of organometallic chemistry, the solution of which should promote more rational use of hydrocarbon raw materials.[1] At the same time, the solution of this problem will allow one to accomplish functionalization of a wide class of compounds containing unactivated C—H bonds.[2] Iridium compounds play an important role here.[3] In the field of study of homogeneous catalysts for dehydrogenation,[4] the most prominent results were achieved using complexes of the type **A** and **B** (see Refs 5—8).

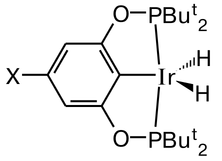
Several years ago, we also began our study on dehydrogenation of alkanes. We succeded in the development of complexes of the type **C** containing pincer ligands based on metallocenes (ferrocene and ruthenocene),[9] which exhibited unprecedent activity in the dehydrogenation of alkanes and at present are the most active catalysts for this reaction.

A necessity to compare electronic and steric properties of the pincer ligands obtained by us with analogous properties of ligands studied by other researches was the reason for the synthesis and more detailed study of chemical properties of complexes of the type B (for example, we described reactions of complex **3** with CO and CNBu^t).

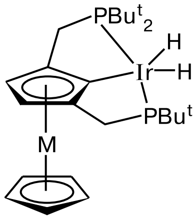
In addition, in order to immobilize dehydrogenation catalysts on polymeric (or dendrimeric) supports we introduced various functional groups (COOR, $CONR_2$, CH_2NR_2) into the pincer ligand of complexes of the type **B**.



A
1, 2



B
3—7



C
8, 9

R = Pr^i (**1**), Bu^t (**2**);
X = H (**3**), Me (**4**), F (**5**), C_6F_5 (**6**), 3,5-(CF_3)$_2C_6H_3$ (**7**);
M = Fe (**8**), Ru (**9**)

In the attempt to modify the substituents indicated, it was found that acidic or basic reagents very often react with the iridium atom instead of a functional group to form a mixture of unidentified products. These observations prompted us to more detailed study of the reaction of known[8] iridium bis(phosphinite) complex **10** and its analogs with various reactive compounds, in particular, with protic acids.

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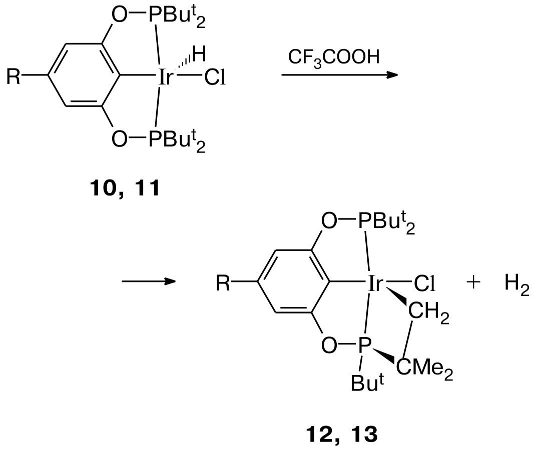
Results and Discussion

We found that complexes **10** and **11** react with hydrochloric acid in THF or with trifluoroacetic acid in CH_2Cl_2 or $CHCl_3$ to yield complexes of the new type. The reaction with CF_3COOH proceeds more smoothly and was studied in details. The reaction of complex **10** takes place at room temperature for several hours, with the formation of complex **12** containing a metallated methyl group of one of the *tert*-butyl substituents at the phosphorus atom as the major product (Scheme 1).

Scheme 1



R = H (**10**, **12**), COOEt (**11**, **13**)

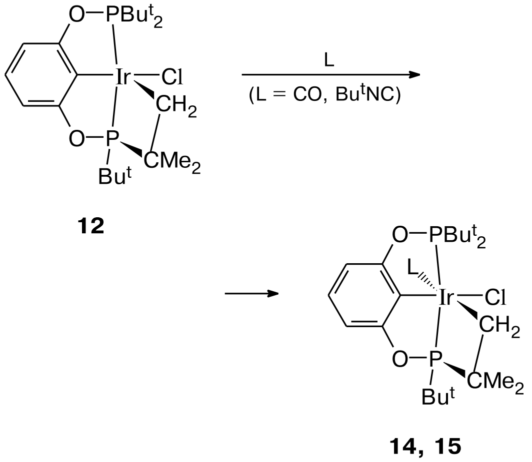
Formation of complex **12** was inferred from the ^{31}P and ^1H NMR spectroscopic data. The ^{31}P NMR spectrum exhibits two doublets at δ 158.5 (d, $J_{P,P}$ = 382.5 Hz) and 117.6 (d, $J_{P,P}$ = 382.5 Hz) from two nonequivalent phosphorus atoms. Note that the spectrum is very similar to the spectrum of the related bis(phosphine) complex published earlier,[10] which was characterized by X-ray diffraction method. In our case, our efforts to apply X-ray diffraction analysis to complex **12** proved unsuccessful due to the strong disorder of the molecules in the crystals obtained. Therefore, conclusions on its structure were made based on the ^{31}P, ^1H, and ^{13}C NMR spectroscopic and elemental analysis data. Thus, for example, the ^1H NMR spectrum exhibits the doublets for the three nonequivalent *tert*-butyl groups, two doublets for the methyl groups of the fragment CMe_2 of the four-membered metallacycle, and two broad multiplet signals for the nonequivalent protons of the methylene group bound with the metal atom.

The $^{13}C\{^1H\}$ NMR spectrum exhibits a doublet signal in the negative region at δ –2.4 (d, $J_{P,C}$ = 25.0 Hz) for the carbon atom of the methylene group bound with the iridium atom. To sum up, the prersence of the analogy between the spectral data for the complexes synthesized by us and described earlier[10] allows one to draw a conclusion on the similarity of their structures.

In the case of complex **11** containing the ester group in the arene ring, the similar reaction with trifluoroacetic acid was also successful: complex **13** was obtained in 79% yield. Note that in this case, the reaction proceeds much slower and requires reflux in chloroform for many hours to be completed.

Complex **12** readily adds such two-electron ligands, as CO and Bu^tNC to form new complexes **14** and **15**, respectively (Scheme 2).

Scheme 2



L = CO (**14**), $CNBu^t$ (**15**)

The 18-electron complexes **14** and **15** obtained were characterized by the ^1H, ^{13}C, and ^{31}P NMR spectroscopic and elemental analysis data. Complex **14** was studied by single-crystal X-ray diffraction analysis, its molecular structure is given in Fig. 1, the main bond distances and bond angles, in Table 1.

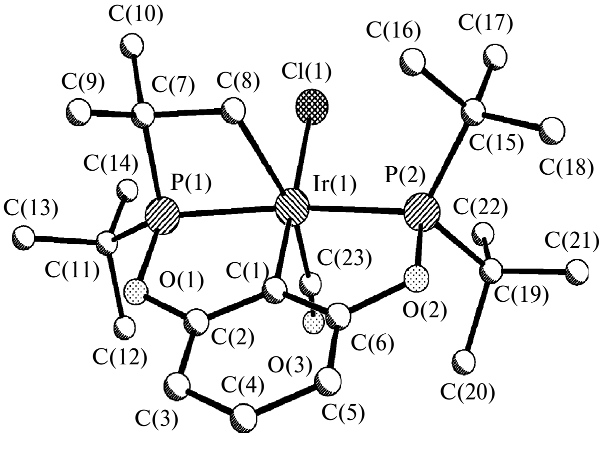


Fig. 1. Molecular structure of complex **14**.

Table 1. The main bond distances (*d*) and bond angles (ω) in complex **14**

Parameter	Value
Bond distance	*d*/Å
Ir(1)—C(1)	2.029(3)
Ir(1)—C(8)	2.172(4)
Ir(1)—P(1)	2.2719(9)
Ir(1)—P(2)	2.3736(9)
Ir(1)—Cl(1)	2.4479(10)
Ir(1)—C(23)	1.910(4)
Angle	ω/deg
C(1)—Ir(1)—Cl(1)	173.7(1)
P(1)—Ir(1)—P(2)	156.93(3)
C(23)—Ir(1)—C(8)	162.3(2)
C(7)—C(8)—Ir(1)	105.8(3)
C(7)—P(1)—Ir(1)	95.0(2)
C(1)—Ir(1)—C(8)	85.0(2)

The structure of **14** is similar to that of complex [4-$MeOC_6H_2$-2-($CH_2PBu^t{}_2$)-6-($CH_2P(Bu^t)CMe_2CH_2$)]-IrCl (**16**) published earlier.[10] The iridium atom is in the distorted octahedron environment. The distance Ir(1)—P(1) is by 0.1 Å shorter than Ir(1)—P(2), which indicates the tightening influence of the four-membered metallacycle. This is also an explaination for the deviation of the phosphorus atom P(1) from the plane of the five-membered chelate ring by 0.21 Å, due to which the chelate ring Ir(1)—P(1)—O(1)—C(2)—C(1) asquires the envelop conformation. At the same time, the second five-membered ring Ir(1)—P(2)—O(2)—C(6)—C(1) is virtually planar (with accuracy of 0.01 Å). The difference in the bond distances Ir(1)—C(8) and Ir(1)—C(1) (0.142 Å) noticeablly differs from that in complex **16** (0.022 Å), which apparently is explained by the *trans*-influence of the CO. The iridium atom virtually lies in the plane of the metallated arene ring (the deviation is 0.012 Å), with the angle P(1)—Ir(1)—P(2) being equal to 156.93(3)°.

It should be noted that only several cases of the formation of complexes similar to **12** and **13** have been described and most of them have been considered in the review published recently.[11] Currently, we direct our efforts on the study of specificities in the mechanism of the reaction discovered by us.

Experimental

All the starting compounds and solvents were purified and dried before the experiments using standard methods. Complex **11** and the corresponding to it bis(phosphinite) precursor were obtained using the Schlenk technique under argon. Ethyl 3,5-dihydroxybenzoate[12] and complex [C_6H_3-2,6-($OPBu^t{}_2)_2$]Ir(H)Cl[8] were synthesized according to the known procedures.

NMR spectra were recorded on a Bruker Avance-600, Bruker Avance-400, and Bruker Avance-300 spectrometers at room temperature, elemental analysis was performed in the Laboratory of Microanalysis of A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

1,3-Bis(di-*tert*-butylphosphinito)-5-ethoxycarbonylbenzene 1,3-($OPBu^t{}_2)_2$-5-(COOEt)C_6H_3. Anhydrous tetrahydrofuran (30 mL) was added to a mixture of ethyl 3,5-dihydroxybenzoate (1.082 g, 5.945 mmol) and 60% NaH in paraffin (0.545 g, 13.625 mmol), the mixture was refluxed for 1 h, after cooling $Bu^t{}_2PCl$ (2.6 mL, 12.964 mmol) was added, followed by reflux for 1 h. Then the reaction mixture was filtered through a celite layer, the celite was washed with dichloromethane (2×5 mL), the solutions were combined and concentrated, the residue was dried *in vacuo*. The product (2.981 g) was obtained as an oil solidifying on standing and containing 0.218 g of mineral oil, the purity was 83% (according to the ^{31}P NMR). It was used for subsequent experiments without further purification. ^{31}P NMR (161.98 MHz, acetone-d_6), δ: 154.9 (s).

Chlorohydrido{2,6-bis(di-*tert*-butylphosphinito)-4-ethoxycarbonylphen-1-yl}iridium(III) [4-$EtOOCC_6H_2$-2,6-($OPBu^t{}_2)_2$]-Ir(H)Cl (11). Diphosphinite (2.981 g, 4.879 mmol), obtained as described above was dissolved in anhydrous toluene (40 mL), followed by addition of $[Ir(COE)_2Cl]_2$ (2.816 g, 3.146 mmol). The reaction mixture was refluxed for 5 h, then concentrated *in vacuo*, the residue was chromatographed on a column with silica gel using a hexane—dichloromethane (1 : 1) mixture as the eluent; a reddish orange fraction collected was concentrated to a small volume and cooled to –20 °C. Crystals formed were filtered off, washed with cold hexane, and dried *in vacuo*. The yield was 2.311 g (68%). ^1H NMR (400.13 MHz, $CDCl_3$), δ: 7.83 (s, 2 H, Ar—H); 4.26 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.1 Hz); 1.34 (m, 36 H, Bu^t); 1.13 (t, 3 H, $—CH_2C\underline{H}_3$, J = 7.1 Hz); –40.03 (t, 1 H, J = 13.0 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$), δ: 176.6 (s). Found (%): C, 42.75; H, 6.35. $C_{25}H_{44}ClIrO_4P_2$. Calculated (%): C, 43.00; H, 6.35.

Reaction of chlorohydrido{2,6-bis(di-*tert*-butylphosphinito)-phen-1-yl}iridium(III) [C_6H_3-2,6-($OPBu^t{}_2)_2$]Ir(H)Cl (10) with CF_3COOH. Trifluoroacetic acid (1 mL) was added to a solution of complex **10** (0.256 g, 0.409 mmol) in dichloromethane (10 mL), the mixture was stirred for 24 h at ~20 °C and concentrated *in vacuo*. The residue was chromatographed on a column with silica gel using a hexane—dichloromethane mixture to elute a red band. The solvent was evaporated, the residue was dried *in vacuo* to obtain chloro{2-di-*tert*-butylphosphinito-6-([*tert*-butyl-2´-(2´,2´-dimethylethylidene)-1´-yl]phosphinito)phen-1-yl}iridium(III) (**12**) (0.144 g, 56%) . ^1H NMR (600.22 MHz, $CDCl_3$), δ: 6.89 (m, 1 H, Ar—H); 6.72 (m, 2 H, Ar—H); 3.01 (dd, 1 H, Ir—CH_2, J = 5.2 Hz, J = 9.6 Hz); 2.03 (s, 1 H, Ir—CH_2); 1.59 (d, 3 H, Ir—CH_2—$C(C\underline{H}_3)_2$, J = 16.7 Hz); 1.51 (d, 9 H, Bu^t, J = 15.5 Hz); 1.29 (d, 9 H, Bu^t, J = 14.7 Hz); 1.20 (d, 9 H, Bu^t, J = 14.0 Hz); 0.97 (d, 3 H, Ir—CH_2—$C(C\underline{H}_3)_2$, J = 12.4 Hz). $^{31}P\{^1H\}$ NMR (242.97 MHz, $CDCl_3$), δ: 158.5 (d, J = 382.5 Hz); 117.6 (d, J = 382.5 Hz). $^{13}C\{^1H\}$ NMR (150.93 MHz, $CDCl_3$), δ: 167.6 (dd, C—O, J = 4.9 Hz, J = 7.6 Hz); 165.3 (dd, C—O, J = 2.8 Hz, J = 6.9 Hz); 126.0 (s, Ar—C); 123.8 (m, Ir—C); 105.3 (d, Ar—C, J = 11.1 Hz); 105.2 (d, Ar—C, J = 11.1 Hz); 66.0 (dd, $\underline{C}Me_3$, J = 5.6 Hz, J = 18.0 Hz); 47.3 (dd, $\underline{C}Me_3$, J = 5.6 Hz, J = 16.6 Hz); 40.9 (t, Ir—CH_2—$\underline{C}Me_2$, J = 9.7 Hz); 39.6 (dd, $\underline{C}Me_3$, J = 5.6 Hz, J = 15.3 Hz); 27.3 (d, $C(\underline{C}H_3)_3$, J = 4.2 Hz); 26.9 (d, $C(\underline{C}H_3)_3$, J = 4.2 Hz); 26.7 (d, $C(\underline{C}H_3)_3$, J = 4.2 Hz); 24.0

(d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 4.2 Hz); 22.1 (d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 2.8 Hz); –2.4 (d, Ir—CH$_2$, *J* = 25.0 Hz). Found (%): C, 42.07; H, 6.10. $C_{22}H_{38}ClIrO_2P_2$. Calculated (%): C, 42.34; H, 6.14.

Reaction of compound 11 with CF_3COOH. Trifluoroacetic acid (0.7 mL) was added to a solution of complex **11** (0.193 g, 0.276 mmol) in chloroform (8 mL), the mixture was refluxed for 17 h and concentrated *in vacuo*. The residue was chromatographed on a column with silica gel using a hexane—dichloromethane mixture to elute a red band. The solvent was evaporated, the residue was dried *in vacuo* to obtain chloro{4-ethoxycarbonyl{2-di-*tert*-butylphosphinito-6-([*tert*-butyl-2´-(2´,2´-dimethylethylidene)-1´-yl]phosphinito)}phen-1-yl}iridium(III) (**13**) (0.152 g, 79%). ^{1}H NMR (300.13 MHz, CDCl$_3$), δ: 7.36 (m, 2 H, Ar—H); 4.35 (q, 2 H, C$\underline{H}_2$Me, *J* = 7.1 Hz); 3.07 (ddd, 1 H, Ir—CH$_2$, *J* = 1.7 Hz, *J* = 5.2 Hz, *J* = 10.1 Hz); 1.90 (m, 1 H, Ir—CH$_2$); 1.57 (d, 3 H, Ir—CH$_2$—C(C$\underline{H}_3$)$_2$, *J* = 16.8 Hz); 1.49 (d, 9 H, Bu^t, *J* = 15.7 Hz); 1.39 (t, 3 H, CH$_2$C$\underline{H}_3$, *J* = 7.1 Hz); 1.27 (d, 9 H, Bu^t, *J* = 14.7 Hz); 1.17 (d, 9 H, Bu^t, *J* = 14.2 Hz); 0.94 (d, 3 H, Ir—CH$_2$—C(C$\underline{H}_3$)$_2$, *J* = 12.5 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, CDCl$_3$), δ: 160.1 (d, *J* = 381.4 Hz); 119.0 (d, *J* = 381.4 Hz). ^{13}C{^{1}H} NMR (100.61 MHz, CDCl$_3$), δ: 167.3 (dd, C—O, *J* = 6.1 Hz, *J* = 7.5 Hz); 166.6 (s, —$\underline{C}$OOCH$_2$Me); 165.0 (dd, C—O, *J* = 3.5 Hz, *J* = 6.8 Hz); 133.5 (m, Ir—C); 128.4 (s, Ar—C); 106.3 (d, Ar—C, *J* = 6.6 Hz); 106.2 (d, Ar—C, *J* = 6.6 Hz); 65.9 (dd, $\underline{C}$Me$_3$, *J* = 4.6 Hz, *J* = 17.8 Hz); 60.6 (s, —O$\underline{C}$H$_2$Me); 47.2 (dd, $\underline{C}$Me$_3$, *J* = 5.3 Hz, *J* = 16.7 Hz); 41.0 (t, Ir—CH$_2$—$\underline{C}$Me$_2$, *J* = 10.0 Hz); 39.6 (dd, $\underline{C}$Me$_3$, *J* = 6.1 Hz, *J* = 15.2 Hz); 27.1 (d, C($\underline{C}$H$_3$)$_3$, *J* = 4.8 Hz); 26.7 (d, C($\underline{C}$H$_3$)$_3$, *J* = 5.1 Hz); 26.5 (d, C($\underline{C}$H$_3$)$_3$, *J* = 4.0 Hz); 23.9 (d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 4.0 Hz); 21.8 (d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 3.3 Hz); 14.3 (s, CH$_2\underline{C}$H$_3$); –1.3 (d, Ir—CH$_2$, *J* = 24.9 Hz). Found (%): C, 42.92; H, 5.90. $C_{25}H_{42}ClIrO_4P_2$. Calculated (%): C, 43.13; H, 6.08.

Chlorocarbonylo{2-di-*tert*-butylphosphinito-6-([*tert*-butyl-2´-(2´,2´-dimethylethylidene)-1´-yl]phosphinito)phen-1-yl}iridium(III) [C_6H_3-2-(OPBu$^t_2$)-6-(OP(Bu^t)CMe$_2$CH$_2$)]Ir(CO)Cl (14). Carbon monoxide was bubbled through a solution of complex **12** (0.036 g, 0.058 mmol) in dichloromethane for 15 min, during which the solution turned colorless. The solvent was evaporated and the residue dried *in vacuo* to obtain complex **14** as a white powder in quantitative yield. ^{1}H NMR (600.22 MHz, CDCl$_3$), δ: 6.85 (virt.t, 1 H, Ar—H, *J* = 8.0 Hz); 6.62 (d, 1 H, Ar—H, *J* = 7.7 Hz); 6.55 (d, 1 H, Ar—H, *J* = 8.0 Hz); 1.90 (ddd, 1 H, Ir—CH$_2$, *J* = 1.4 Hz, *J* = 8.9 Hz, *J* = 10.3 Hz); 1.63 (d, 3 H, Ir—CH$_2$—C(C$\underline{H}_3$)$_2$, *J* = 19.7 Hz); 1.47—1.42 (m, 18 H, Bu^t); 1.29 (d, 9 H, Bu^t, *J* = 14.6 Hz); 1.09 (d, 3 H, Ir—CH$_2$—C(C$\underline{H}_3$)$_2$, *J* = 15.3 Hz); 0.84 (m, 1 H, Ir—CH$_2$). ^{31}P{^{1}H} NMR (242.97 MHz, CDCl$_3$), δ: 153.8 (d, *J* = 333.2 Hz); 87.3 (d, *J* = 333.2 Hz). ^{13}C{^{1}H} NMR (100.61 MHz, CDCl$_3$), δ: 173.3 (d, C—O, *J* = 6.9 Hz); 162.2 (d, C—O, *J* = 6.0 Hz); 125.6 (s, Ar—C); 116.2 (m, Ir—C); 106.4 (d, Ar—C, *J* = 9.9 Hz); 105.6 (d, Ar—C, *J* = 9.9 Hz); 62.3 (dd, $\underline{C}$Me$_3$, *J* = 6.9 Hz, *J* = 27.6 Hz); 44.0 (dd, $\underline{C}$Me, *J* = 8.6 Hz, *J* = 12.9 Hz); 42.1 (dd, $\underline{C}$Me$_3$, *J* = 3.2 Hz, *J* = 15.3 Hz); 36.8 (t, Ir—CH$_2$—$\underline{C}$Me$_2$, *J* = 10.3 Hz); 30.2 (d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 4.3 Hz); 28.6 (d, C($\underline{C}$H$_3$)$_3$, *J* = 4.7 Hz); 28.1 (d, —C($\underline{C}$H$_3$)$_3$, *J* = 4.3 Hz); 25.5 (d, C($\underline{C}$H$_3$)$_3$, *J* = 3.0 Hz); 25.1 (d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 4.7 Hz); 14.6 (dd, Ir—CH$_2$, *J* = 3.0 Hz, *J* = 36.6 Hz). IR (CH$_2$Cl$_2$), ν/cm^{-1}: 2017 (CO). Found (%): C, 42.31; H, 5.91. $C_{23}H_{38}ClIrO_3P_2$. Calculated (%): C, 42.36; H, 5.87.

Chloro(*tert*-butylisonitrilo){2-di-*tert*-butylphosphinito-6-([*tert*-butyl-2´-(2´,2´-dimethylethylidene)-1´-yl]phosphinito)phen-1-yl}iridium(III) [C_6H_3-2-(OPBu$^t_2$)-6-(OP(Bu^t)CMe$_2$CH$_2$)]-Ir(CNBu^t)Cl (15). *tert*-Butyl isonitrile (0.1 mL) was added to a solution of complex **12** (0.031 g, 0.050 mmol) in dichloromethane and the mixture was stirred for 15 min, during which the solution turned colorless. The solvent was evaporated and the residue dried *in vacuo* to obtain complex **15** as a white powder in quantitative yield. ^{1}H NMR (300.13 MHz, CDCl$_3$), δ: 6.75 (m, 1 H, Ar—H); 6.50 (m, 2 H, Ar—H); 1.82 (m, 1 H, Ir—C$\underline{H}_2$, *J* = 8.8 Hz, *J* = 12.6 Hz); 1.59 (d, 3 H, Ir—CH$_2$—C(C$\underline{H}_3$)$_2$, *J* = 19.2 Hz); 1.44—1.40 (m, 27 H, Bu^t + CNBu^t); 1.27 (d, 9 H, Bu^t, *J* = 14.3 Hz); 1.02 (d, 3 H, Ir—CH$_2$—C(C$\underline{H}_3$)$_2$, *J* = 14.3 Hz); 0.64 (m, 1 H, Ir—CH$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, CDCl$_3$), δ: 150.8 (d, *J* = 363.0 Hz); 89.7 (d, *J* = 363.0 Hz). ^{13}C{^{1}H} NMR (150.93 MHz, CDCl$_3$), δ, principal signals: 167.1, 163.1 (dd, C—O, *J* = 5.8 Hz, *J* = 59.1 Hz); 123.8 (s, Ar—C); 118.5 (m, Ir—C); 105.4 (d, Ar—C, *J* = 10.4 Hz); 105.4 (d, Ar—C, *J* = 9.8 Hz); 62.5, 56.9, 44.3, 42.3 (dd, $\underline{C}$Me$_3$, *J* = 4.2 Hz, *J* = 13.4 Hz); 36.6, 30.6 (s, CN—C($\underline{C}$H$_3$)$_3$); 30.1 (d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 5.2 Hz); 28.9 (d, C($\underline{C}$H$_3$)$_3$, *J* = 5. Hz); 26.2 (d, C($\underline{C}$H$_3$)$_3$, *J* = 3.2 Hz); 25.1 (d, Ir—CH$_2$—C($\underline{C}$H$_3$)$_2$, *J* = 5.2 Hz); 9.34 (dd, Ir—CH$_2$, *J* = 2.9 Hz, *J* = 35.5 Hz). Found (%): C, 45.78; H, 6.84; N, 2.02. $C_{27}H_{47}ClIrNO_2P_2$. Calculated (%): C, 45.85; H, 6.70; N, 1.98.

X-ray diffraction study of complex 14. Crystals **14** ($C_{23}H_{38}O_3ClP_2Ir$, M = 652.12) are monoclinic, the space group is $P2_1/n$, at 298 K a = 15.6873(8) Å, b = 11.3096(6) Å, c = 16.2266(9) Å, β = 114.158(1)°, V = 2626.7(2) Å^3, Z = 4, d_{calc} = 1.649 g cm^{-3}, μ(Mo-Kα) = 53.27 cm^{-1}. Intensities of 30726 reflections (6950 independent reflections, R_{int} = 0.0277) were measured on a Bruker SMART APEX II diffractometer with a coordinate detector[13] (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω-scanning, $2\theta_{\max}$ = 58°, T = 298 K). Semiempirical allowance for absorption was made using the SADABS program.[14] The structure was solved by the direct method and refined by the full-matrix least squares method on F^2_{hkl} with anisotropic thermal parameters for all the nonhydrogen atoms. The hydrogen atoms were placed into the geometrically calculated positions and included in refinement in the riding model. The final divergence factors: R_1 = 0.0249 (refinement on F_{hkl} for 5568 reflections with $I > 2\sigma(I)$), wR_2 = 0.0619 and S = 1.082 (refinement on F^2_{hkl} for all the independent reflections). The calculations were performed using the SHELXTL program package.[15] The full Tables of atom coordinates, bond distances, bond angles, and anisotropic thermal parameters were deposited with the Cambridge Structural Database.

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