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### Synthesis and characterization of fluorophenylpalladium pincer complexes: electronic properties of some pincer ligands evaluated by multinuclear NMR spectroscopy and electrochemical studies<sup>†</sup>

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Palladium fluorophenyl complexes with different pincer ligands  $Pd(Ar)[2,6-(tBu_2PCH_2)_2C_6H_3]$  (13),  $Pd(Ar)[2,6-(tBu_2PO)_2C_6H_3]$  (14),  $Pd(Ar)[\{2,5-(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$  (15), and  $Pd(Ar)[\{2,5-(tBu_2PCH_2)_2C_5H_2\}Ru(C_5H_5)]$  (16) were synthesized by the reaction of LiAr (Ar =  $C_6H_4F$ -4) with the respective trifluoroacetate palladium pincer complexes 9–12. The molecular structures of 14 and 16 were determined by an X-ray crystallographic method. Complexes 13–16 and  $\{Pd(Ar)[\{2,5-(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}PF_6$  (17) were studied by multinuclear NMR spectroscopy and cyclic voltammetry. On the basis of <sup>19</sup>F NMR chemical shifts and <sup>1</sup> $J(^{13}C^{-19}F)$  coupling constants, as well as  $Pd^{II}/Pd^{IV}$  oxidation potentials, electronic characteristics of the corresponding pincer ligands were elucidated.

#### Introduction

Pincer complexes of transition metals have intensively been studied over the past several decades because of their ability to catalyze a wide range of chemical reactions.<sup>1</sup> Especially impressive results were achieved for iridium pincer complexes (Chart 1), which catalyze selective alkane dehydrogenation, a challenging transformation of saturated hydrocarbons and one of the most significant tasks of organic chemistry and homogeneous catalysis.<sup>2</sup> Following pioneer works of Crabtree<sup>3a-c</sup> and Felkin<sup>3d,e</sup> on stoichio-

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Taking into account not only the fundamental, but also the practical importance of homogeneous catalytic alkane dehydrogenation,<sup>2</sup> considerable efforts have been undertaken to investigate mechanistic details of catalytic alkane dehydrogenation by iridium pincer complexes, using both experimental<sup>5d-g,6c,8a</sup> and computational methods.<sup>5d-g,9</sup> Apparently, the catalytic activity of



R = tBu, X = H (1a), OMe (1b), COOMe (1c), NMe<sub>2</sub> (1d) R = iPr, X = H (1e), OMe (1f)



R = tBu, X = OMe (2a), Me (2b), H (2c)F (2d), C<sub>6</sub>F<sub>5</sub> (2e), 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (2f)



M = Fe, 3 M = Ru, 4

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the systems considered should be affected by both a steric factor (the accessibility of the catalytic center for a substrate), and an electronic factor, *i.e.* the relative electron density at the iridium atom. It is recognized that the steric accessibility of the iridium atom is determined by the bulkiness of the organyl R groups of the phosphorous donor atoms<sup>8</sup> and by the value of the P–Ir–P angle in the pincer complex.<sup>7</sup> Evaluation of the electronic factor appeared to be more complex. This ambiguity became apparent during comparison of the electronic effects of the two benzene-based ligands, bis(phosphine)<sup>8a</sup> and bis(phosphinite)<sup>6</sup> pincers.

In spite of using experimental and computational methods, it is still not clear how the electronic properties of the bis(phosphine) pincer ligand change when methylene CH<sub>2</sub> groups in it are replaced with oxygen atoms. Thus, based on the measurement of the carbonyl stretching frequencies vCO of the respective CO adducts Ir(CO)[2,6-(tBu<sub>2</sub>PO)<sub>2</sub>-4-X-C<sub>6</sub>H<sub>2</sub>] (Ir(CO)[PO,C,OP-X], 2), Brookhart and co-workers<sup>6b</sup> supposed that bis(phosphinite) pincer ligands are significantly less electron-donating than their bis(phosphine) counterparts. On the other hand, computational results obtained by Goldman and co-workers<sup>8a</sup> showed that the thermodynamic and kinetic properties are affected in the same directions, relative to the parent P,C,P ligand, by the presence of the *p*-methoxy substituent and by the substitution of the ligand methylene groups bound to phosphorus with the oxygen atoms (to form a PO.C, OP ligand) even though these substitutions affect the vCO values in opposite directions. Calculations also showed that the iridium atom in bis(phosphinite) complexes bears a comparable or even more negative charge than in the bis(phosphine) counterparts and the higher vCO value of Ir(CO)[PO,C,OP] is most likely attributable to electrostatic effects.8a,10

Since a deep understanding of ligand electronic characteristics is necessary for rational catalyst design, it is desirable to clarify the electronic properties of different pincer ligands by the use of experimental methods other than  $\nu$ CO values measurement.

<sup>19</sup>F NMR chemical shifts in aryl fluorides have been found to be a sensitive tool for the examination of substituent electronic effects. These chemical shifts correlate with the resonance effects of *para* substituents in *para*-disubstituted fluorobenzenes and with the inductive effects of *meta* substituents in *meta*-disubstituted fluorobenzenes.<sup>11</sup> Applications of this method to organometallic systems are exemplified by the measurements of <sup>19</sup>F NMR chemical shifts of *meta*- and *para*- fluorophenyl derivatives of nickel, palladium and platinum phosphine complexes<sup>12</sup> as well as transition and non-transition metal fluorophenylcyclopentadienyls.<sup>13</sup>

Herein, we report the synthesis of *p*-fluorophenylpalladium pincer complexes for <sup>19</sup>F NMR and electrochemical studies of the electronic properties of different pincer ligands. The complexes studied include bis(phosphine) and bis(phosphinite) benzene-based and bis(phosphine) ferrocene- and ruthenocene-based pincers. The results obtained are compared with the existing literature data on electronic properties of the pointed ligands.

#### **Results and discussion**

### Synthesis and characterization of *p*-fluorophenyl derivatives of palladium pincer complexes

Initial palladium chloride complexes with benzene and metallocene backbones, compounds 5, 7, and 8, were synthesized according to the literature procedures.<sup>14–16</sup> Novel complex **6** was obtained by cyclopalladation of 1,3-( $tBu_2PO$ )<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.<sup>6a</sup> It was found that palladium chlorides PdCl[<sup>R</sup>P,C,P] are not good candidates for nucleophilic substitution reaction,<sup>17</sup> therefore to facilitate the reaction with the appropriate lithium reagent they were converted to the corresponding palladium trifluoroacetates (Scheme 1). Thallous trifluoroacetate was used instead of CF<sub>3</sub>COOAg in the case of the metallocene complexes to avoid metallocene oxidation which is likely to occur at least with the ferrocene-based complex.



Fluorophenyl derivatives of palladium pincer complexes were synthesized by methods similar to those reported by Milstein<sup>18</sup> and Wendt<sup>19</sup> for the preparation of Pd(Ph)[<sup>Pr</sup>P,C,P] and Pd(Ph)[<sup>PBu</sup>P,C,P], respectively. Treatment of **9–12** with LiC<sub>6</sub>H<sub>4</sub>F-4 gives the corresponding fluorophenyl derivatives **13–16** in yields from low to moderate (Scheme 2).

The reaction is complicated by formation of the appropriate PdBr[P,C,P] complexes (LiC<sub>6</sub>H<sub>4</sub>F-4 is generated from BrC<sub>6</sub>H<sub>4</sub>F-4 and this results in the presence of bromine-containing species in the reaction mixture) and decomposition of the lithium reagent, which impedes the purification. Compounds 13-16 were fully characterized by means of multinuclear NMR spectroscopy and elemental analysis; complexes 14 and 16 were also studied by the X-ray diffraction method. Typical <sup>1</sup>H NMR spectroscopic features of 13 and 14 show a virtual triplet and overlapping doublet of doublets for hydrogens meta and ortho with respect to the fluorine atom in the case of benzene-based complexes; for metallocene-based complexes all hydrogens within the Pd-C<sub>6</sub>H<sub>4</sub>F-4 fragment became non-equivalent and appear as virtual triplets or multiplets. The  ${}^{31}P{}^{1}H{}$  and  ${}^{19}F$  NMR spectra of compounds 13–16 exhibit singlets; *ipso* carbon resonance of the Pd-C<sub>6</sub>H<sub>4</sub>F-4 fragment undergoes splitting on both fluorine and phosphorus nuclei thus appearing as triplet of doublets in the  ${}^{13}C{}^{1}H$  NMR spectra.

The molecular structures of **14** and **16** are illustrated in Fig. 1 and Fig. 2. In both compounds, the palladium atom has a distorted square-planar geometry with the fluorobenzene ring being virtually perpendicular to the plane of the benzene (94.8°) or the cyclopentadienyl (90.8°) ring of the pincer backbones. The Pd–C(1) distance in **16** (2.006(2) Å) is slightly shorter then in **14** (2.031(2) Å); similar differences in the Ir–C(1) lengths were







Fig. 1 Molecular structure of 14 (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 2.031(2), Pd(1)–C(11) 2.078(2), Pd(1)–P(1) 2.2794(6), Pd(1)–P(2) 2.2835(6), C(1)–Pd(1)–C(11) 174.23(9), C(1)–Pd(1)–P(1) 79.79(7), C(1)–Pd(1)–P(2) 79.64(7), P(1)–Pd(1)–P(2) 158.63(2).

reported for the iridium carbonyl derivatives of the corresponding pincer complexes<sup>7</sup> (2.025 Å for Ir(CO)[<sup>*rBu*</sup>P,C,P<sup>Fe</sup>] *vs.* 2.046 for Ir(CO)[<sup>*rBu*</sup>PO,C,OP]).

Contrary to Pd–C(1), the distance between Pd and the *ipso* carbon atom of the fluorophenyl group for **16** (2.104(2) Å) is longer than for **14** (2.078(2) Å) which may indicate a stronger *trans* influence of the ruthenocene-based pincer ligand.



Fig. 2 Molecular structure of 16 (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 2.006(2), Pd(1)–C(11) 2.104(2), Pd(1)–P(1) 2.3247(5), Pd(1)–P(2) 2.3253(5), C(1)–Pd(1)–C(11) 171.41(7), C(1)–Pd(1)–P(1) 80.11(5), C(1)–Pd(1)–P(2) 80.16(5), P(1)–Pd(1)–P(2) 157.15(2).

For the sake of comparison, we oxidized **15** using  $[Cp_2Fe]PF_6$  to give the cationic compound **17** (Scheme 3). Although this paramagnetic complex reveals broad signals in the region of 33 to -118 ppm in the <sup>1</sup>H NMR spectrum, in <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F spectra sufficiently sharp signals are observed at  $\delta$  94.2 (s) from two equivalent phosphorus atoms, and -152.9 ppm (septet,



Scheme 3

	<i>v</i> CO (cm <sup>-1</sup> )		
Compound	Hydrocarbon solution	CH <sub>2</sub> Cl <sub>2</sub> solution	
Ir(CO)[ <sup>7Bu</sup> P,C,P <sup>Fe</sup> ]	1926 <sup>a</sup>	1904 <sup><i>d</i></sup>	
$Ir(CO)[^{rBu}P,C,P^{Ru}]$	1926 <sup>a</sup>	1905 <sup>d</sup>	
$\{Ir(CO)[^{tBu}P,C,P^{Fe}]\}PF_6$		1951 <sup>d</sup>	
$Ir(CO)[2,6-(tBu_2PCH_2)_2C_6H_3]$	1928 <sup>b</sup>	1913 <sup>e</sup>	
$Ir(CO)[2,6-(tBu_2PO)_2C_6H_3]$	1949 <sup>c</sup>	1938 <sup>e</sup>	

<sup>*a*</sup> Hexane solution, ref. 7. <sup>*b*</sup> Cyclooctane solution, ref. 5*c*. It should be noted that in the very recent article, ref. 20, the value of the 1914 cm<sup>-1</sup> is given for a hexane solution of this complex. Such a marked difference between two measurements in saturated hydrocarbon solvents is unexpected and needs further investigation. <sup>*c*</sup> Pentane solution, ref. 6*b*. <sup>*d*</sup> Ref. 7. <sup>*e*</sup> Present work.

J = 711.4 Hz) from a PF<sub>6</sub> anion, respectively. Previously it was found that {PdCl[<sup>*i*Bu</sup>P,C,P<sup>Fe</sup>]}PF<sub>6</sub> reveals a singlet at  $\delta$  93.9 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum.<sup>15</sup>

## Comparison of the <sup>19</sup>F NMR chemical shifts. Electronic properties of the pincer ligands

The existing approach for evaluation of electronic properties of different pincer ligands is based on the measurement of the vCO stretching frequencies of the respective iridium CO adducts. The literature and our data is shown in Table 1.

This approach was criticised on the basis of the results obtained by the computational methods as exemplified by comparison of the bis(phosphine) and bis(phosphinite) benzene-based pincer complexes.<sup>8a</sup> The calculations showed that the iridium atom in bis(phosphinite) complexes bears a comparable or even more negative charge than that in bis(phosphine) analogues and the higher vCO value for Ir(CO)[PO,C,OP] is most likely attributable to electrostatic effects.<sup>8a,10</sup> In fact, substitution of the ligand methylene groups bound to phosphorus with the oxygen atoms (to form PO,C,OP) in the parent P,C,P ligand has two opposite effects: oxygen atoms withdraw electron density from the phosphorous atoms due to an inductive effect and donate electron density to the benzene ring by resonance effect. As such, it is difficult to conclude which effect will predominate in dictating electron density at the metal atom.

It is believed that <sup>19</sup>F NMR chemical shifts of aryl fluorides correlate with electronic properties of substituents in the benzene ring. The lower the frequency of the <sup>19</sup>F chemical shift is, the more electron density substituent donates to the benzene ring. <sup>19</sup>F chemical shifts of complexes **13–17** are listed in Table 2.

 Table 2
 <sup>19</sup>F NMR parameters for complexes 13–17

$^{19}$ F NMR chemical shifts" (ppm)/ $^{1}J$ ( $^{13}$ C– $^{19}$ F) coupling constants (Hz)	
$C_6D_6$ solution	CD <sub>2</sub> Cl <sub>2</sub> solution
11.60	12.67/236.6
10.47	11.49/237.1
11.98	13.11/235.7
11.90	13.08
—	12.95
	$\frac{{}^{19}\text{F NMR chemica}}{C_6 D_6 \text{ solution}}$ 11.60 10.47 11.98 11.90 -

<sup>*a*</sup> Upfield with respect to fluorobenzene.

Chemical shifts were measured against an internal fluorobenzene standard in two solvents,  $C_6D_6$  and  $CD_2Cl_2$ . <sup>19</sup>F NMR chemical shifts in Table 2 indicate an upfield resonance with respect to  $C_6H_5F$ . Also, the values of the spin–spin coupling constants  ${}^{1}J({}^{13}C{}^{-19}F)$  are given in Table 2. It is known<sup>21</sup> that a satisfactory correlation exists between  ${}^{19}F$  NMR chemical shifts and spin–spin coupling constants  ${}^{1}J({}^{13}C{}^{-19}F)$ , with coupling constant decreasing while shielding of the fluorine nucleus rises. This inverse dependence of fluorine nuclei shielding from  ${}^{1}J({}^{13}C{}^{-19}F)$ values was also demonstrated on several organometallic derivatives of *p*-fluorophenylcyclopentadienyl compounds.<sup>22</sup> As can be seen from Table 2, this correlation exists for *p*-fluorophenyl derivatives of the palladium pincer complexes studied.

It is evident from the data presented in Table 2 that there is apparent difference in <sup>19</sup>F nuclei shielding between the benzene-based bis(phosphinite) complex **14** and the bis(phosphine) complex **13** while changes in fluorine chemical shifts among bis(phosphine) complexes **13**, **15** and **16** are less pronounced. According to these data, the lowest relative electron density should belong to the palladium atom in the bis(phoshinite) complex **14**. If we assume that <sup>19</sup>F NMR chemical shifts correctly reflect the relative electron density at a metal atom in different type pincer complexes, it is interesting to compare this data with *v*CO values given in Table 1 (see Fig. 3).



**Fig. 3** Linear correlation, with **17** excluded, of the  $\nu$ CO frequencies and <sup>19</sup>F NMR chemical shifts.

A linear least squares solution through the points corresponding to **13–16** gives  $vCO = 2177.99 - 20.89*\delta$  with a correlation coefficient of 0.999. Apparently, complex **17** deviates strongly from this line. This fact should be preferably attributed to the paramagnetic nature of the compound **17**. In this case, it is likely that a contribution from the paramagnetic center affects the <sup>19</sup>F shielding in spite of it being remote from the Fe atom, and the <sup>19</sup>F NMR chemical shift fails to correctly reflect the electron density at the Pd center. Indeed, both *v*CO and Pd<sup>II</sup>/Pd<sup>IV</sup> oxidation potentials (see below) show a dramatic decrease in the donating ability of the pincer ligand, while according to the <sup>19</sup>F NMR chemical shifts this changes only slightly and the Pd atom in **17** is almost as electron-rich as in the neutral complex **15**, which is pretty unrealistic.

Thus, it appears that the <sup>19</sup>F NMR and vCO probes produce comparable information for this series of compounds. Note that

the p-orbital belonging to the C-ipso of the C<sub>6</sub>H<sub>4</sub>F-4 unit is virtually orthogonal to that of the benzene/Cp rings and they cannot overlap with the same orbital of the Pd atom. Hence,  $\pi$ effects caused by the pincer ligand are transmitted to the C<sub>6</sub>H<sub>4</sub>F-4 more indirectly and probably can be underestimated, while in the case of the respective Ir-CO adducts direct conjugation between the C-ipso and CO orbitals through the Ir atom is possible. However, taking into consideration the sufficiently good correlation mentioned above, it may be suggested that the  $\pi$ -effects of substituents in pincer ligands do not play the major role in dictating electron density at the metal atom. In fact, we suppose that, although <sup>19</sup>F NMR and vCO probes measure quite different things, for the compounds presented they both mainly reflect the ligand electronic effects being transmitted to the metal atom through inductive/field mechanisms with resonance effects being insufficient. That's why the existence of some correlation between <sup>19</sup>F chemical shifts and vCOs is possible, however it is dangerous to ascribe much significance to such dependence. In particular, for the PO,C,OP vs. P,C,P pair resonance effect of the oxygen atoms is not competitive with their  $\sigma$  electron withdrawing ability. For example, replacement of a hydrogen in a para position with the methoxy group in Ir(CO)[<sup>fBu</sup>P,C,P] and Ir(CO)[<sup>fBu</sup>PO,C,OP] only leads to a 2 cm<sup>-1</sup> red shift in comparison with parent compounds (1947 cm<sup>-1</sup> for Ir(CO)[PO,C,OP-4-OMe]<sup>6b</sup> and 1926 cm<sup>-1</sup> for Ir(CO)['<sup>Bu</sup>P,C,P-4-OMe]<sup>8a</sup>) due to the resonance effect of the –OMe group. At the same time, the CO stretching frequency is much more sensitive to inductive/field effects produced by substituents at P atoms: substitution of the ligand methylene groups bound to phosphorus with the oxygen atoms (to form PO,C,OP) leads to ca. 20 cm<sup>-1</sup> blue shift despite the resonance effect of the oxygens (about 4 cm<sup>-1</sup> in the opposite direction if one rather crudely assumes ortho and para effects are comparable). Even more dramatic changes occur when tBu groups are replaced with  $CF_3$ . Thus, the vCO for the recently published complex Ir(CO)[CF3P,C,P]23 is 105 cm<sup>-1</sup> greater than for Ir(CO)[<sup>rBu</sup>P,C,P]. Such behavior can be explained by electrostatic effects,<sup>8a,10</sup> however we do think in these cases vCOs correctly reflect electron density at the metal atom. Indeed, the presence of, for example, a methoxy group obviously substantially changes the nature of the  $\pi$ -system of an aryl ligand, but the extent to which this effect is transmitted to the metal atom seems to be rather small. For example, in terms of both trans influence and trans effect phenyl and p-anisyl are quite similar.<sup>24</sup> Besides, during a study concerning metal-containing groups as substituents in benzene, a number of *m*- and *p*-fluorophenyl transition metal complex  $\sigma_{I}$  and  $\sigma_{\rm R}$  constants were determined; in contrast to inductive parameters, resonance parameters varied over a small range for rather different complexes, and in related series of compounds  $(e.g., -Mn(CO)_{5-x})$  $L_x$ , or  $-Pt(PEt_3)_2X$ ) they were almost invariant. It was concluded that these minor changes in  $\sigma_{R}$  reflect the relative unimportance of  $\pi$ -bonding to the aryl ring relative to other ligands.<sup>25</sup>

#### Cyclic voltammetry

In order to verify conclusions made from NMR spectroscopy we undertook an electrochemical study of complexes **13**, **14** and **15**. Cyclic voltammograms were recorded in a CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub> 9:1 mixture. For all pincer complexes an irreversible oxidation wave was observed, which we attribute to Pd<sup>II</sup>/Pd<sup>IV</sup> oxidation. Oxidation potentials are listed in Table 3 and in general fall into

Table 3  $Pd^{II}/Pd^{IV}$  oxidation potentials as measured by cyclic voltammetry<sup>*a*</sup>

Compound (Ar = $C_6H_4Fp$ )	$E^{\mathrm{ox}} \left(\mathrm{Fe^{II}}/\mathrm{Fe^{III}}\right) \left(\mathrm{V}\right)$	$E^{\mathrm{ox}}(\mathrm{Pd}^{\mathrm{II}}/\mathrm{Pd}^{\mathrm{IV}})$ (V)
PdAr[ <sup><i>f</i>Bu</sup> P,C,P] ( <b>13</b> ) PdAr[ <sup><i>f</i>Bu</sup> PO,C,OP] ( <b>14</b> ) PdAr[ <sup><i>f</i>Bu</sup> P,C,P <sup>Fe</sup> ] ( <b>15</b> )	-0.10	0.60 0.83 1.17

<sup>*a*</sup> Conditions: glassy carbon electrode, scan rate 200 mV s<sup>-1</sup>, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in 9:1 CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub> mixture, Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> as internal reference.

the range obtained by van Koten *et al.* for related P,C,P, S,C,S and N,C,N palladium pincer complexes.<sup>26</sup> Note that for complex **15**, two redox processes were observed. The first redox process was a reversible peak at -0.10 V which corresponds to one-electron oxidation of the Fe atom and is close to that for PdCl[<sup>*r*bu</sup>P,C,P<sup>Fe</sup>].<sup>15</sup> The second redox process was observed at a more positive potential of 1.17 V and corresponds to the irreversible Pd<sup>II</sup>/Pd<sup>IV</sup> oxidation. In fact, we can consider this second process as an oxidation of the *in situ* generated complex **17**.

It is evident from Table 3 that electrochemical data supports the conclusions made from spectroscopic methods. Thus, bis(phoshinite) complex 14 undergoes oxidation at a sufficiently higher potential ( $\Delta E^{ox} = 230 \text{ mV}$ ) than its bis(phosphine) counterpart 13 which indicates that the Pd atom in 14 is less electron-rich. Oxidation of the central atom of the metallocene makes a direct comparison of complex 15 with 13 and 14 by electrochemistry impossible; however, the strong electron-withdrawing effect of the Fe-oxidized ligand in 17 could be observed. If we take  $E_{ox}$  for 13 as a rough measure for the hypothetical 15 Pd-based oxidation (vCO and  $\delta^{19}$ F are rather close for these compounds), oxidation of the ferrocene unit nearly doubles the  $E^{ox}$ .

Remarkably, three experimental methods showed the same trends in the estimation of the relative donor ability of the pincer ligands. At the same time, the data obtained here support our conclusion that the higher catalytic activity of complexes **2**, **3**, and **4** in alkane dehydrogenation *versus* that of complex **1** have mainly steric reasons.<sup>7</sup> Thus, compounds **2**, **3**, and **4** have a smaller P–Ir–P angle than **1**, which provides a higher accessibility of the Ir atom for a substrate, while there is clear a similarity in the electronic properties of the pincer ligands in complexes **1** and **3**, **4**. It should be noted that recent DFT calculations gave further evidence to the fact that the metal center of Ir(CO)[<sup>rBu</sup>PO,C,OP] is much less sterically hindered than that of Ir(CO)[<sup>rBu</sup>P,C,P], which results in improved catalytic activity.<sup>27</sup>

#### Conclusions

To summarize, we have prepared a series of new *p*-fluorophenylpalladium complexes with four different pincer ligands. The measurement of the <sup>19</sup>F NMR parameters and Pd<sup>II</sup>/Pd<sup>IV</sup> oxidation potentials allowed us to make some conclusions on the electron density at the palladium atoms and the electronic properties of the appropriate ligands, which correlate well with previously reported data based on *v*CO stretching frequencies of iridium carbonyl complexes with the same pincer ligands. On the basis of <sup>19</sup>F NMR parameters, Pd<sup>II</sup>/Pd<sup>IV</sup> oxidation potentials of palladium *p*-fluorophenyl pincer complexes and *v*CO frequencies of iridium carbonyl adducts, the donor ability of pincer ligand follows the order:  $[{}^{tBu}P,C,P^{Fe+}]^-$ ,  $[2,6-(tBu_2PO)_2C_6H_3]^-$ ,  $[2,6-(tBu_2PCH_2)_2C_6H_3]^-$ ,  $[{}^{tBu}P,C,P^{Ru}]^-$  and  $[{}^{tBu}P,C,P^{Fe}]^-$ .

#### Experimental

#### **General considerations**

All manipulations on the synthesis of pincer ligands and complexes were conducted under an argon atmosphere using standard Schlenk techniques. Resulting compounds 5-17 are air-stable and their purification doesn't require an inert atmosphere. All solvents were distilled under an argon atmosphere from the appropriate drying agents. Commercially available reagents were used as received. Compounds PdCl[2,6- $(tBu_2PCH_2)_2C_6H_3$ ] (5),<sup>14</sup> PdCl[{2,5- $(tBu_2PCH_2)_2C_5H_2$ }Fe(C<sub>5</sub>H<sub>5</sub>)] (7),<sup>15</sup> and PdCl[{2,5-(*t*Bu<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>2</sub>}Ru(C<sub>5</sub>H<sub>5</sub>)] (8)<sup>16</sup> were prepared according to the literature procedures. NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are reported in parts per million downfield from tetramethylsilane; the residual signals of deuterated solvents were used as references (7.26 ppm for CDCl<sub>3</sub>, 7.16 ppm for  $C_6D_6$ , 5.32 ppm for  $CD_2Cl_2$ ). In  ${}^{13}C{}^{1}H{}$  NMR measurements the signal of  $CD_2Cl_2$  (53.7 ppm) was used as a reference. <sup>19</sup>F{<sup>1</sup>H} chemical shifts are reported relative to internal fluorobenzene for compounds 13-17 and to external CFCl<sub>3</sub> for others.  ${}^{31}P{}^{1}H$  NMR chemical shifts are reported relative to an external 85% solution of phosphoric acid in D<sub>2</sub>O. Assignments of signals in the <sup>1</sup>H NMR spectra of 15 and 16 were made using NOESY spectrum. FTIR spectra were recorded on a Nicolet Magna-IR 750 Fourier spectrometer. Elemental analyses were performed at the A.N. Nesmeyanov Institute of Organoelement Compounds of RAS. Despite several attempts, satisfactory elemental analysis for the ruthenium-containing complexes 15 and 16 was not obtained. The products, however, appeared to be analytically pure, as indicated by NMR.

Synthesis of  $PdCl[2,6-(tBu_2PO)_2C_6H_3]$  (6). To a suspension of NaH (0.700 g, 17.500 mmol, 60% dispersed in mineral oil) in 60 ml of THF was added solution of resorcinol (0.870 g, 7.909 mmol) in 15 ml of THF. The mixture was heated to reflux for 1 h, then tBu<sub>2</sub>PCl (3.5 ml, 18.440 mmol) was added and the mixture was refluxed for an additional 1 h. The volatiles were removed in vacuum, the residue was dissolved in 50 ml of 2-methoxyethanol and after addition of Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (2.950 g, 7.702 mmol) refluxed for 3 h. The pre-cooled reaction mixture was filtered through Celite and the filtrate was evaporated in vacuum. The residue was purified using column chromatography on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub>-hexane 1:1) and crystallised from a CH<sub>2</sub>Cl<sub>2</sub>-hexane mixture. Yield: 1.307 g (31%). Found: C, 49.04; H 7.19. Calc. for C<sub>22</sub>H<sub>39</sub>ClO<sub>2</sub>P<sub>2</sub>Pd: C, 48.99; H, 7.29. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>):  $\delta$  6.95 (tt, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz,  ${}^{5}J_{PH} = 1.1$  Hz, 1H, Ar–H), 6.53 (d,  ${}^{3}J_{HH} = 8.0$  Hz, 2H, Ar– H), 1.43 (m, 36H, 4 *t*Bu). <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, CDCl<sub>3</sub>): δ 192.1.

General procedure for the syntheses of palladium trifluoroacetates 9–12. Excess of  $CF_3COOAg$  or  $CF_3COOTI$  was added to a solution of 5–8 in the appropriate quantity of THF. The reaction mixture was stirred for 3 h and then filtered through a short silica gel column (alumina was used instead in the case of metallocenebased compounds 11 and 12). Until this stage, the reaction mixture should be protected from light. The column was washed by  $CH_2Cl_2$ and the resulting solution was concentrated in vacuum followed by addition of hexane and cooling to -20 °C. The solution was decanted and the solid was washed with hexane and dried under vacuum.

**Pd(TFA)**[2,6-( $tBu_2PCH_2$ )<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (9). Starting from 0.265 g (1.199 mmol) of CF<sub>3</sub>COOAg and 0.585 g (1.094 mmol) of 5 0.535 g (80%) of 9 was obtained. NMR spectra and elemental analysis are in agreement with literature data.<sup>19,28</sup>

**Pd(TFA)**[2,6-( $tBu_2PO$ )<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (10). Starting from 0.259 g (1.172 mmol) of CF<sub>3</sub>COOAg and 0.602 g (1.118 mmol) of 6 0.467 g (68%) of **10** was obtained. NMR spectra and elemental analysis are in agreement with literature data.<sup>29</sup>

**Pd(TFA)**[<sup>*f*B</sup>**P**,**C**,**P**<sup>*f*e</sup>] (11). Starting from 0.390 g (1.230 mmol) of CF<sub>3</sub>COOT1 and 0.450 g (0.700 mmol) of **7** 0.409 g of **11** was obtained. According to NMR spectra, the sample contains ~25% of the starting chloride **7** and was not subjected to elemental analysis. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  4.24 (s, 2H, C<sub>3</sub>H<sub>2</sub>), 3.96 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 2.92 (t, <sup>1</sup>J<sub>HH</sub> = 15.2 Hz, 2H, CH<sub>A</sub>CH<sub>B</sub>P), 2.51 (dt, <sup>1</sup>J<sub>HH</sub> = 16.7 Hz, <sup>3</sup>J<sub>PH</sub> = 4.6 Hz, 2H, CH<sub>A</sub>CH<sub>B</sub>P), 1.57 (vt, *J* = 7.1 Hz, 2 *t*Bu) 1.29 (vt, *J* = 6.6 Hz, 2 *t*Bu). <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, CDCl<sub>3</sub>):  $\delta$  85.4. <sup>19</sup>F{<sup>1</sup>H} NMR (282.40 MHz, CDCl<sub>3</sub>):  $\delta$  -75.33.

**Pd(TFA)**[<sup>*Bu*</sup>**P,C,P<sup>Ru</sup>**] (12). Starting from 0.480 g (1.514 mmol) of CF<sub>3</sub>COOT1 and 0.333 g (0.484 mmol) of **8** 0.223 g (60%) of **12** was obtained. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ 4.62 (s, 2H, C<sub>5</sub>H<sub>2</sub>), 4.40 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 2.71 (dt, <sup>1</sup>J<sub>HH</sub> = 16.7 Hz, <sup>3</sup>J<sub>PH</sub> = 3.1 Hz, 2H, CH<sub>A</sub>CH<sub>B</sub>P), 2.58 (dt, <sup>1</sup>J<sub>HH</sub> = 16.7 Hz, <sup>3</sup>J<sub>PH</sub> = 4.4 Hz, 2H, CH<sub>A</sub>CH<sub>B</sub>P), 1.34 (two overlapping vt,  $J_1 = 6.7$  Hz,  $J_2 = 7.3$  Hz, 4 *t*Bu) <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, CDCl<sub>3</sub>): δ 84.4. <sup>19</sup>F{<sup>1</sup>H} NMR (282.40 MHz, CDCl<sub>3</sub>): δ -75.39.

General procedure for the syntheses of palladium *p*-fluorophenyls 13–16. A solution of  $\text{LiC}_6\text{H}_4\text{F}$ -4 in  $\text{Et}_2\text{O}$  was added dropwise to a suspension of complexes 9–12 in  $\text{Et}_2\text{O}$ ; the reaction mixture was brought to room temperature and stirred overnight. After addition of water, the layers were separated and the aqueous layer was twice extracted with  $\text{Et}_2\text{O}$ . The combined organic layers were dried over MgSO<sub>4</sub> and the volatiles were evaporated in vacuum. The residue was purified by column chromatography and recrystallisation.

 $LiC_6H_4F-4^{30}$ . It was prepared according to the literature procedure from  $BrC_6H_4F-4$  and used immediately after preparation. To a stirred solution of butyllithium (3.0 ml; 1.6 M in hexane) in diethyl ether (10 ml) at -30 °C was added dropwise 1-bromo-4-fluorobenzene (0.50 ml, 4.551 mmol) in diethyl ether (10 ml). Then the reaction mixture was stirred for 45 min and brought to room temperature.

 $Pd(C_6H_4F-p)[2,6-(tBu_2PCH_2)_2C_6H_3]$  (13). The reaction was conducted with 0.535 g (0.874 mmol) of 9 and LiAr prepared from 0.50 ml (4.551 mmol) of  $BrC_6H_4F$ -4 as described above. After column chromatography on silica gel using hexane– $CH_2Cl_2 5:1$  as an eluent and crystallisation from hexane– $CH_2Cl_2 0.103$  g (20%) of 13 was obtained as a white powder. An additional 0.014 g (3%) of pure compound 13 was yielded by repetitive chromatography of the residue from the fractions left after first chromatography containing trace amounts of 13. Found: C, 60.09; H, 8.25. Calc. for C<sub>30</sub>H<sub>47</sub>FP<sub>2</sub>Pd: C, 60.55; H, 7.96. <sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.64 (vt, J = 8.0 Hz, 2H, 8- and 12-H), 7.05 (d,  ${}^{3}J_{\rm HH} = 7.4$  Hz, 2H, 3- and 5-H), 6.91 (t,  ${}^{3}J_{\rm HH} = 7.4$  Hz, 1H, 4-H), 6.75 (dd,  ${}^{3}J_{\rm HH} =$ 8.0 Hz,  ${}^{3}J_{\rm HF} = 10.1$  Hz, 2H, 9- and 11-H), 3.47 (m, 4H, 2 CH<sub>2</sub>), 1.19 (vt, J = 6.8 Hz, 36H, 4 *t*Bu).  ${}^{13}C{}^{1}H$  NMR (100.61 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 173.59 (t,  ${}^{3}J_{\rm CP} = 3.3$  Hz, 1-C), 160.35 (d,  ${}^{1}J_{\rm CF} = 236.6$  Hz, 10-C), 158.04 (td, J = 4.0 Hz, J = 12.3 Hz, 7-C), 150.86 (vt, J =9.7 Hz, 2- and 6-C), 142.75 (m, 8- and 12-C), 124.60 (s, 4-C), 120.64 (vt, J = 9.2 Hz, 3- and 5-C), 112.00 (d,  ${}^{2}J_{\rm CF} = 16.1$  Hz, 9and 11-C), 38.96 (vt, J = 10.8 Hz, 2 CH<sub>2</sub>), 35.74 (vt, J = 7.3 Hz, 4  $C({\rm CH}_{3})_{3}$ ), 29.68 (vt, J = 2.9 Hz,  $C({\rm CH}_{3})_{3}$ ).  ${}^{31}{\rm P}{}^{1}{\rm H}$  NMR (121.49 MHz, C<sub>6</sub>D<sub>6</sub>): δ 71.7.  ${}^{19}{\rm F}{}^{1}{\rm H}$  NMR (282.40 MHz, C<sub>6</sub>D<sub>6</sub>): δ 11.60.



 $Pd(C_6H_4F-p)[2,6-(tBu_2PO)_2C_6H_3]$  (14). The reaction was conducted with 0.607 g (0.985 mmol) of 10 and LiAr prepared from 0.43 ml (3.914 mmol) of BrC<sub>6</sub>H<sub>4</sub>F-4 as described above. After column chromatography on silica gel using hexane-CH<sub>2</sub>Cl<sub>2</sub> 3:1 as an eluent and crystallisation from hexane-CH<sub>2</sub>Cl<sub>2</sub> 0.250 g (42%) of 14 was obtained as a white powder. Found: C, 56.18; H, 7.23. Calc. for C<sub>28</sub>H<sub>43</sub>FO<sub>2</sub>P<sub>2</sub>Pd: C, 56.14; H, 7.24. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.65 (vt, J = 7.7 Hz, 2H, 8- and 12-H), 7.09–6.98 (m, 3H, 4-, 9- and 11-H), 6.83 (d,  ${}^{3}J_{HH} = 7.7$  Hz, 2H, 3- and 5-H), 1.16 (vt, J = 7.3 Hz, 36H, 4 tBu). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz,  $CD_2Cl_2$ ): 166.52 (vt, J = 6.2 Hz, 2- and 6-C), 160.52 (d,  ${}^1J_{CF} =$ 237.1 Hz, 10-C), 154.90 (td, J = 4.0 Hz, J = 11.8 Hz, 7-C), 141.65 (m, 8- and 12-C), 140.27 (m, 1-C), 127.68 (s, 4-C), 112.85 (d,  ${}^{2}J_{CF} =$ 16.9 Hz, 9- and 11-C), 104.66 (vt, J = 6.5 Hz, 3- and 5-C), 39.89 (vt, J = 8.1 Hz, 4  $C(CH_3)_3$ ), 27.94 (vt, J = 3.7 Hz,  $C(CH_3)_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, C<sub>6</sub>D<sub>6</sub>): δ 191.4. <sup>19</sup>F{<sup>1</sup>H} NMR (282.40 MHz, C<sub>6</sub>D<sub>6</sub>): δ 10.47.



 $Pd(C_6H_4F-p)[^{rBu}P,C,P^{Fe}]$  (15). The reaction was conducted with 0.409 g (ca. 0.438 mmol of 11 and 0.146 mmol of 9) of 11 and LiAr prepared from 0.25 ml (2.276 mmol) of BrC<sub>6</sub>H<sub>4</sub>F-4 as described above. After column chromatography on alumina using hexane-Et<sub>2</sub>O 5:1 as an eluent and crystallisation from hexane 0.069 g of 15 was obtained as an orange powder in a 17% yield with respect to the overall molar amount of the reagents. Found: C, 57.91; H, 7.39. Calc. for C<sub>34</sub>H<sub>51</sub>FFeP<sub>2</sub>Pd: C, 58.09; H, 7.31. <sup>1</sup>H NMR (400.13 MHz,  $CD_2Cl_2$ ):  $\delta$  7.78 (vt, J = 7.6 Hz, 1H, 7-H), 7.57 (vt, J = 7.6 Hz, 1H, 11-H), 6.81 (vt, J = 8.2 Hz, 1H, 8-H), 6.71 (vt, J = 9.1 Hz, 1H, 10-H), 4.28 (s, 1H, C<sub>5</sub>H<sub>2</sub>), 3.94 (s, 5H,  $C_5H_5$ ), 3.08 (d,  $J_{HH}$  = 16.6 Hz, 2H,  $CH_ACH_BP$  endo), 2.66 (dt,  $J_{\rm HH} = 16.6$  Hz,  $J_{\rm HP} = 4.0$  Hz, 2H, CH<sub>A</sub>CH<sub>B</sub>P exo), 1.21 (vt, J =6.3 Hz, 18H, 2 *t*Bu *exo*), 1.16 (vt, *J* = 6.8 Hz, 18H, 2 *t*Bu *endo*). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 162.91 (m, 6-C), 160.24  $(d, {}^{1}J_{CF} = 235.7 \text{ Hz}, 9\text{-C}), 143.08 \text{ (s) and } 141.22 \text{ (s, 7-C and } 11\text{-C}),$ 124.00 (m, 1-C), 112.02 (d,  ${}^{2}J_{CF}$  = 16.2 Hz) and 111.95 (d,  ${}^{2}J_{CF}$  = 15.8 Hz, 8-C and 10-C), 93.50 (vt, J = 13.3 Hz, 2- and 5-C), 70.36

(s, C<sub>5</sub>H<sub>2</sub>), 64.88 (vt, J = 7.9 Hz, 3- and 4-C), 36.92 (vt, J = 5.8 Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 35.06 (vt, J = 6.6 Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 30.25 (vt, J = 2.9 Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 28.93 (vt, J = 3.4 Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 28.82 (vt, J = 11 Hz, 2 CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  71.7. <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  86.2. <sup>19</sup>F{<sup>1</sup>H} NMR (282.40 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  11.98.



 $Pd(C_6H_4F-p)[^{rBu}P,C,P^{Ru}]$  (16). The reaction was conducted with 0.407 g (0.532 mmol) of 12 and LiAr prepared from 0.22 ml (2.003 mmol) of BrC<sub>6</sub>H<sub>4</sub>F-4 as described above. After column chromatography on alumina using hexane-Et<sub>2</sub>O 5:1 as an eluent and crystallisation from hexane 0.060 g (15%) of 16 was obtained as a yellowish powder. <sup>1</sup>H NMR (300.13 MHz,  $CD_2Cl_2$ ):  $\delta$  7.69 (vt, J = 7.7 Hz, 1H, 7-H), 7.56 (vt, J = 7.5 Hz, 1H, 11-H), 6.80–6.65 (m, 2H, 8- and 10-H), 4.70 (s, 1H, C<sub>5</sub>H<sub>2</sub>), 4.35 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 2.90 (d,  $J_{\rm HH}$  = 16.6 Hz, 2H,  $CH_{\rm A}CH_{\rm B}P$  endo), 2.77 (dt,  $J_{\rm HH}$  = 16.5 Hz,  $J_{\rm HP} = 4.1$  Hz, 2H, CH<sub>A</sub>CH<sub>B</sub>P exo), 1.28 (vt, J = 6.4 Hz, 18H, 2 *t*Bu *exo*), 1.08 (vt, J = 6.9 Hz, 18H, 2 *t*Bu *endo*). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 162.38 (m, 6-C), 160.22 (d,  ${}^{1}J_{CF} \approx 235$  Hz (this value is very approximate due to inappropriate acquisition of the spectrum and is not included in Table 2), 9-C), 143.12 (s) and 141.40 (s, 7- and 11-C), 126.51 (t,  $J_{CP} = 5.8$  Hz, 1-C), 111.98 (d,  ${}^{2}J_{CF} = 15.9$  Hz) and 111.89 (d,  ${}^{2}J_{CF} = 15.9$  Hz, 8- and 10-C), 97.51 (vt, J = 13.7 Hz, 2- and 5-C), 71.77 (s, C<sub>5</sub>H<sub>2</sub>), 68.06 (vt, J = 7.9 Hz, 3- and 4-C), 36.81 (vt, J = 5.8 Hz, 2  $C(CH_3)_3$ ), 34.67 (vt, J = 6.7 Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 30.26 (vt, J = 2.9 Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 28.89  $(vt, J = 3.4 Hz, 2 C(CH_3)_3), 28.76 (vt, J = 11.3 Hz, 2 CH_2)^{.31} P{^1H}$ NMR (161.98 MHz,  $C_6D_6$ ):  $\delta$  85.3. <sup>19</sup>F{<sup>1</sup>H} NMR (282.40 MHz, C<sub>6</sub>D<sub>6</sub>): δ 11.90.



 $\{Pd(C_6H_4F-p)[^{rBu}P,C,P^{Fe}]\}PF_6$  (17). To a solution of 0.0060 g (0.0085 mmol) of 15 in dichloromethane (7 ml) was added 0.0027 g (0.0082 mmol) of [Cp<sub>2</sub>Fe]PF<sub>6</sub>. The reaction mixture was stirred for 1 h which was accompanied by a color change from orange to green. Volatiles were removed in vacuum and the residue was twice washed with small portions of a hexane-benzene 1:1 mixture and dried in vacuum. Compound 17 was obtained as a green powder (0.0069 g, 91%). Found: C, 46.66; H, 5.76. Calc. for  $C_{34}H_{51}F_7FeP_3Pd \times 0.5CH_2Cl_2$ : C, 46.54; H, 5.89. <sup>1</sup>H NMR (400.13) MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 33.00 (br, 2H, C<sub>5</sub>H<sub>2</sub>), 22.97 (br, 5H, C<sub>5</sub>H<sub>5</sub>), 7.71 (s, 1H, Ar-H), 6.92 (s, 18 H, 2 tBu), 5.51 (s, 1H, Ar-H), 4.02 (s, 1H, Ar-H), 0.89 (s, 1H, Ar-H), -9.89 (s, 18H, 2 tBu), -28.27 (s, 2H,  $CH_{A}CH_{B}P$ ), -118.08 (s, 2H,  $CH_{A}CH_{B}P$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz,  $C_6D_6$ ):  $\delta$  94.2 (s, 2P, 2 *t*Bu<sub>2</sub>P), -152.9 (sept,  ${}^1J_{PF} = 711.4$  Hz, 1P, PF<sub>6</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (282.40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -35.50 (d, <sup>1</sup>J<sub>PF</sub> = 711.4 Hz, 6F, PF<sub>6</sub>), 12.95 (s, 1F, ArF).

Table 4	Crystal data, data collection and structure refinement parameters
or comp	blexes 14 and 16

Complex	14	16
Formula	$C_{28}H_{43}FO_2P_2Pd$	$C_{34}H_{51}FP_2PdRu$
Molecular weight	598.96	748.16
Crystal dimension/mm	$0.30 \times 0.20 \times 0.15$	$0.24 \times 0.13 \times 0.07$
Crystal system	Triclinic	Triclinic
Space group	P1	PĪ
a/Å	8.3067(5)	10.5669(7)
b/Å	10.6772(6)	10.6045(7)
c/Å	17.3068(10)	15.8685(10)
$\alpha /^{\circ}$	93.176(1)	100.877(1)
$\beta/^{\circ}$	99.251(1)	96.133(1)
$\gamma/^{\circ}$	109.389(1)	107.634(1)
$V/Å^3$	1419.3(1)	1638.4(2)
Ζ	2	2
$d(calc.), g cm^{-3}$	1.402	1.517
$\theta_{\max}$ (°).	28.0	29.0
$\mu/\mathrm{cm}^{-1}$	7.96	11.35
Transmission, $T_{\min}/T_{\max}$	0.775/0.890	0.801/0.941
No. unique refls $(R_{int})$	6719 (0.0300)	8639 (0.0268)
No. obs. refls $(I > 2\sigma(I))$	5783	7533
$R_1$ (on F for obs. refls) <sup>a</sup>	0.0330	0.0242
$wR_2$ (on $F^2$ for all refls) <sup>b</sup>	0.0718	0.0570
GOF	1.021	1.006
${}^{a}R_{1} = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o} $	$^{b} wR_{2} = \{ \Sigma [w(F_{a}^{2} - F_{a}^{2})] \}$	$\left(\frac{2}{2}\right)^{2} \left(\sum_{n=1}^{\infty} w(F_{n}^{2})^{2}\right)^{1/2}$

#### X-ray diffraction study of 14 and 16

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite monochromated Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\omega$ -scan technique, T = 100(2)K). The APEX II software<sup>31</sup> was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL<sup>32</sup> for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F2 with the anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation. The principal experimental and crystallographic parameters are presented in Table 4.

#### Notes and references

- The Chemistry of Pincer Compounds; D. Morales-Morales and C. M. Jensen, ed.; Elsevier: Amsterdam, The Netherlands, 2007.
- R. G. Bergman, *Nature*, 2007, **446**, 391–393; (*b*) B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154–162; (*c*) A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879–2932; (*d*) R. H. Crabtree, *J. Chem. Soc.*, *Dalton Trans.*, 2001, 2437–2450.
- 3 (a) R. H. Crabtree, J. M. Mihelcic and J. M. Quirk, J. Am. Chem. Soc., 1979, 101, 7738–7740; (b) M. J. Burk, R. H. Crabtree, C. P. Parnell and R. J. Uriarte, Organometallics, 1984, 3, 816–817; (c) M. J. Burk and R. H. Crabtree, J. Am. Chem. Soc., 1987, 109, 8025–8032; (d) M. J. Baudry, M. Ephritikine, H. Felkin and R. Holmes-Smith, J. Chem. Soc., Chem. Commun., 1983, 788–789; (e) H. Felkin, T. Fillebeen-Khan, R. Holmes-Smith and Y. Lin, Tetrahedron Lett., 1985, 26, 1999–2000.
- 4 (a) M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1996, 2083–2084; (b) M. Gupta, C. Hagen, W. C.

Kaska, R. E. Cramer and C. M. Jensen, *J. Am. Chem. Soc.*, 1997, **119**, 840–841; (c) C. M. Jensen, *Chem. Commun.*, 1999, 2443–2449.

- F. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, J. Am. Chem. Soc., 1999, 121, 4086–4087; (b) W-W. Xu, G. P. Rosini, M. Gupta, C. M. Jensen, W. C. Kaska, K. Krogh-Jespersen and A. S. Goldman, Chem. Commun., 1997, 2273–2274; (c) F. Liu and A. S. Goldman, Chem. Commun., 1999, 655–656; (d) K. Krogh-Jespersen, M. Czerw and A. S. Goldman, J. Mol. Catal. A: Chem., 2002, 189, 95–110; (e) K. Krogh-Jespersen, M. Czerw, K. Zhu, B. Singh, M. Kanzelberger, N. Darji, P. D. Achord, K. B. Renkama and A. S. Goldman, J. Am. Chem. Soc., 2002, 124, 10797–10809; (f) K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord and A. S. Goldman, J. Am. Chem. Soc., 2002, 124, 11404–11416; (g) K. B. Renkema, Y. V. Kissin and A. S. Goldman, J. Am. Chem. Soc., 2003, 125, 7770– 7771.
- 6 (a) I. Göttker-Schnetmann, P. S. White and M. Brookhart, J. Am. Chem. Soc., 2004, 126, 1804–1811; (b) I. Göttker-Schnetmann, P. S. White and M. Brookhart, Organometallics, 2004, 23, 1766–1776; (c) I. Göttker-Schnetmann and M. Brookhart, J. Am. Chem. Soc., 2004, 126, 9330–9338.
- 7 S. A. Kuklin, A. M. Sheloumov, F. M. Dolgushin, M. G. Ezernitskaya, A. S. Peregudov, P. V. Petrovskii and A. A Koridze, *Organometallics*, 2006, 25, 5466–5476.
- 8 (a) K. Zhu, P. D. Achord, X. Zhang, K. Krogh-Jespersen and A. S. Goldman, J. Am. Chem. Soc., 2004, **126**, 13044–13053; (b) S. Kundu, Y. Choliy, G. Zhuo, R. Ahuja, T. J. Emge, R. Warmuth, M. Brookhart, K. Krogh-Jespersen and A. S. Goldman, Organometallics, 2009, **28**, 5432–5444.
- 9 (a) S. Li and M. B. Hall, Organometallics, 2001, **20**, 2153–2160; (b) H.-J. Fan and M. B. Hall, J. Mol. Catal. A: Chem., 2002, **189**, 111–118.
- 10 A. S. Goldman and K. Krogh-Jespersen, J. Am. Chem. Soc., 1996, 118, 12159–12166.
- 11 (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen and G. T. Davis, J. Am. Chem. Soc., 1963, 85, 3146–3156; (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen and G. T. Davis, J. Am. Chem. Soc., 1963, 85, 709–724; (c) C. Hansch, A. Leo and R. W. Taft, Chem. Rev., 1991, 91, 165–195.
- 12 G. W. Parshall, J. Am. Chem. Soc., 1974, 96, 2360-2366.
- (a) A. A. Koridze, S. P. Gubin, A. A. Lubovich, B. A. Kvasov and N. A. Ogorodnikova, *J. Organomet. Chem.*, 1971, **32**, 273–277; (b) S. P. Gubin, A. A. Koridze, N. A. Ogorodnikova, A. A. Bezrukova and B. A. Kvasov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1981, 1170–1172; (c) T. E. Bitterwolf and A. C. Ling, *J. Organomet. Chem.*, 1977, **141**, 355–370.
- 14 C. J. Moulton and B. L. Shaw, J. Chem. Soc., Dalton Trans., 1976, 1020–1024.
- 15 A. A. Koridze, S. A. Kuklin, A. M. Sheloumov, F. M. Dolgushin, V. Yu. Lagunova, I. I. Petukhova, M. G. Ezernitskaya, A. S. Peregudov, P. V. Petrovskii, E. V. Vorontsov, M. Baya and R. Poli, *Organometallics*, 2004, 23, 4585–4593.
- 16 S. A. Kuklin, F. M. Dolgushin, P. V. Petrovskii and A. A. Koridze, *Russ. Chem., Bull. Int. Ed.*, 2006, 55, 1950–1955.
- 17 J. Campora, P. Palma, D. del Rio and E. Alvarez, *Organometallics*, 2004, 23, 1652–1655.
- 18 M. Ohff, A. Ohff, M. E. van der Boom and D. Milstein, J. Am. Chem. Soc., 1997, 119, 11687–11688.
- 19 R. Johansson, M. Jarenmark and O. F. Wendt, *Organometallics*, 2005, 24, 4500–4502.
- 20 B. Punji, T. J. Emge and A. S. Goldman, Organometallics, 2010, 29, 2702–2709.
- 21 J. D. Roberts and F. J. Weigert, J. Am. Chem. Soc., 1971, 93, 2361– 2369.
- 22 A. A. Koridze, P. V. Petrovskii, A. S. Peregudov and N. A. Ogorodnikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2612–2613.
- 23 J. J. Adams, N. Arulsamy and D. M. Roddick, *Organometallics*, 2011, 30, 697–711.
- 24 (a) O. F. Wendt, A. Oskarsson, J. G. Leipoldt and L. I. Elding, *Inorg. Chem.*, 1997, 36, 4514–4519; (b) M. Schmulling, A. D. Ryabov and R. J. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1994, 1257–1263; (c) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207–2215.
- 25 R. P. Stewart and P. M. Treichel, J. Am. Chem. Soc., 1970, 92, 2710– 2718.
- 26 (a) S. Bonnet, M. Lutz, A. L. Spek, G. van Koten and R. J. M. K. Gebbink, *Organometallics*, 2010, **29**, 1157–1167; (b) S. Bonnet, J. H. van Lenthe, M. A. Siegler, A. L. Spek, G. van Koten and R. J. M. K.

Gebbink, Organometallics, 2009, **28**, 2325–2333; (c) M. Gagliardo, G. Rodriguez, H. H. Dam, M. Lutz, A. L. Spek, R. W. A. Havenith, P. Coppo, L. De Cola, F. Hartl, G. P. M. van Klink and G. van Koten, *Inorg. Chem.*, 2006, **45**, 2143–2155.

- 27 J. Choi, A. H. R. MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761–1779.
- 28 M. E. van der Boom, S. Liou, Y. Ben-David, L. J. W Shimon and D. Milstein, J. Am. Chem. Soc., 1998, 120, 6531–6541.
- 29 R. Johansson and O. F. Wendt, Dalton Trans., 2007, 488-492.
- 30 M. del P. Crespo, T. D. Avery, E. Hanssen, E. Fox, T. V. Robinson, P. Valente, D. K. Taylor and L. Tilley, *Antimicrob. Agents Chemother.*, 2008, 52, 98–109.
- 31 APEX II software package, Bruker AXS Inc., 5465, East Cheryl Parkway Madison, WI 5317, 2005.
- 32 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2007, 64, 112–122.