

Remote C-F-Metal Interactions in Late-Transition-Metal Complexes

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A series of phosphorus ligands containing the 5,6,7,8-tetrafluoronaphthalen-1-yl group (NpF₄) has been prepared, starting from 1-bromo-5,6,7,8-tetrafluoronaphthalene. The coordination chemistry of diphenyl(5.6,7.8-tetrafluoronaphthalen-1-vl)phosphine (1) with Ir(III), Pd(II), Pt(II), Rh(I), Ir(I), and Au(I) has been investigated, focusing on a possible remote interaction of the fluorine atom at position 8 of the naphthyl group (F^1) with the metal center. The Ir(III) complex [IrCp*Cl₂(1)] (12) displays a weak $J(\mathbf{P}, \mathbf{F}^{1})$ coupling constant of 8 Hz and no Ir- \mathbf{F}^{1} interaction. A cationic derivative, the formally coordinatively unsaturated $[IrCp*Cl(1)]SbF_6$ (13), is generated upon chloride abstraction. For this complex $J(P,F^1)$ is 80 Hz and the $Ir-F^1$ distance is 2.956(2) Å. [MCl(η^3 -allyl)(1)] complexes (14, M = Pt; 15, M = Pd) display what is interpreted as a weaker $M-F^1$ interaction despite corresponding $J(P,F^1)$ values of 67 and 98 Hz and $M-F^1$ distances of 3.069(2) and 2.995(2) Å, respectively. Similar considerations apply to the analogous Rh(I) and Ir(I) complexes [IrCl(COD)(1)] (18) and [RhCl(COD)(1)] (19) $(J(P,F^{1}) = 62 \text{ and } 75 \text{ Hz and } M-F^{1} = 3.0744(14) \text{ and } 3.0997(8) \text{ Å},$ respectively). With the chiral enantiopure ligand (11bS)-4-(5,6,7,8-tetrafluoronaphthalen-1yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine (10) analogous complexes were prepared. Ligand 10 is formally a derivative of 1 where the two phenyl groups have been replaced by a BINOL unit. In the case of $[PtCl(\eta^3-allyl)(10)]$ (16) and [RhCl(COD)(10)] (21) the coupling between F¹ and the NMRactive nuclei ¹⁹⁵Pt and ¹⁰³Rh, respectively, was detected in 2D NMR heteronuclear correlation experiments.

Introduction

Glusker's first detailed and systematic search in the Cambridge Structural Database (CSD) for exceptionally short $CF \cdots$ metal distances (for group 1 and 2 metals) in 1983 led to the conclusion that "the CF bond is capable of significant, if not prominent, interactions with both alkaline metal cations and proton donors".¹ Though the relevance of this topic was put forward by Glusker, only scattered reports appeared initially in the literature and the investigation of such "remote" $CF \cdots$ metal interactions mainly focused on group 1 and 2 metal cations, since it was reasoned that the hard fluorine atom (categorized by the HSAB principle²) would preferably interact with hard metal cations. Thus, systematic investigations mainly of group 1 and 2 metals

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were carried out by Plenio³⁻⁶ and Takemura,⁷⁻⁹ who used X-ray analysis and stability constant measurements as well as NMR spectroscopy (mainly the ${}^{1}J(C,F)$ coupling constant, the ${}^{19}F$ chemical shift, and ${}^{6.7}Li/{}^{107,109}Ag/{}^{133}Cs/{}^{205}Tl-{}^{19}F$ direct coupling) as means for the detection of such interactions in the case of monofluorinated cryptands and crown ethers. In 1997, Plenio reviewed the complete work on CF···metal interactions and defined for the first time a set of criteria for a CF···M interaction to be accepted as such.³ For instance, it was pointed out that a minimum of four bonds must separate the metal from the remote fluorine, thus ruling out complexes of fluorinated ligands such as $-C_6F_5$, η^6 - C_6F_6 , $-CF_3$, $=CF_2$, and $F_2C=CF_2$. Plenio argued that "It is very possible that the presence of fluorine in the complexes of such ligands is stabilizing, but it should also be considered that such contacts are the unavoidable result of the existence of such metal complexes."3 Furthermore, it was stated that a comparison of the investigated $M \cdots F$ distance with the sum of the corresponding van der Waals radii appears to be too loose a criterion for the judgment of an interaction. Instead, Plenio suggested the use of the ionic van der Waals radii for group 1 and 2 metals (for typical coordination numbers). Thus, for a $M \cdots F$ distance to be considered as a significant interaction, an overall threshold of ≤ 2.7 Å was set for first-row transition metals, a value smaller than the sum of the van der

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Figure 1. Collection of reported metal complexes showing $CF \cdots M$ interactions.

Waals radii. Applying the same principle to second- and thirdrow transition metals results in a threshold of \leq 3.0 Å.

A brief overview of the most relevant substructures of recurring ligands and metals that have been used for the study of the coordination chemistry of the CF unit is shown in Figure 1.

It turns out that late second- and third-row transition metals are underrepresented, and four examples of welldocumented complexes are depicted in Figure 2. Ruthenium has been repeatedly reported to interact with CF units. Perera and Shaw¹⁰ ascribed the large J(P,F) coupling constant of 68 Hz observed for complex A in Figure 2 to a Ru-F interaction. Grubbs¹¹ attributed the enhanced performance of a ring-closing metathesis catalyst (B) to the existence of a Ru-F interaction and found Ru-F distances as short as 2.5203(12) Å in certain cases. Another short Ru-F distance of 2.489(6) Å was reported by Cruz-Garritz.^{12,13} Crabtree¹⁴ found an exceptionally short Ir-F distance and used NMR data, i.e. the large J(F,H) coupling constant, to corroborate the hypothesis of a M-F interaction (C). Already in 1987, Cavell¹⁵ explained the unexpectedly high J(Pt,F) coupling constant in complex **D** by the spatial proximity of fluorine to platinum, which "allows facile van der Waals penetration" and leads to "through space spin-spin coupling".¹⁵

Although this collection of examples is not complete, it already covers the most important work done in the field of $CF \cdots M$ interactions for late transition metals, thus also revealing the paucity of data in this area.

In the present work, we expanded the scope of transition metals possibly undergoing a remote M-F interaction by utilizing new phosphorus ligands containing the 5,6,7,8-tetrafluoronaphthalen-1-yl group (NpF₄). In these ligands

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Figure 2. Examples of late second- and third-row transition metals, where the $CF \cdots M$ interaction has been proven by X-ray diffraction analysis and/or NMR spectroscopy.

the P and F atoms undergoing an interaction with the metal center are separated by four bonds in a rigid, planar framework. Some methodologies for the detection of the $CF \cdots M$ interactions have also been adapted to this very purpose. In particular, to the best of our knowledge, rare 2D fluorinemetal NMR correlation spectra have been used for the first time in this field. It will also become clear that the nature of the $CF \cdots$ metal interaction very much depends on the metal, its oxidation state, and its ligand environment.

Results and Discussion

During our efforts to prepare new phosphorus ligands containing the NpF₄ group to be used in transition-metalcatalyzed reactions, we observed an interesting NMR spectroscopic property of such compounds. Indeed, the ³¹P and the ¹⁹F NMR spectra show an unexpected, very strong coupling between phosphorus and the fluorine atom at position 8 of the naphthyl fragment, here indicated for simplicity as F^{1} . This behavior is commonly referred to as "through-space coupling", 16-18 indicating that it does not primarily take place via the bonds of the connecting carbon framework. A better term would be "through-lone-pair coupling", since this arises from the fact that the phosphorus lone pair has a nonvanishing spatial probability density overlapping with the fluorine lone pair or even encompassing the ¹⁹F nucleus.¹⁹ Thus, a series of different P-NpF₄ derivatives containing various substituents at phosphorus have been prepared by standard procedures, starting from 1-bromo-5,6,7,8-tetrafluoronaphthalene.²⁰ These compounds, together with their corresponding J(P,F) values, are shown in Table 1. Depending on the two remaining substituents on phosphorus, the J(P,F) coupling constant can be as high as 324 Hz for Cl_2P-NpF_4 (9). Note for comparison that the J(P,F) value for a P-CF₃ group, for

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compd	R^1	\mathbb{R}^2	$J(\mathbf{P},\mathbf{F})$ (Hz)
1	Ph	Ph	198
2	Ph	$N(Et)_2$	200
3	Ph	NpF ₄	213
4 (<i>rac</i>)	Ph	CF_3	219
5 ^{<i>a</i>}	NpF_4	NpF_4	232
6 $(S)^{b}$	Pĥ	O(1R)-menthyl	242
$7(R)^{b}$	O-(1 R)-menthyl	Ph	246
8 ^a	Cl	NpF_4	282
9 ^{<i>a</i>}	Cl	CÎ	324
10	0,0'-(S)-BINOL	250	
11	O,O'-(R,R)-Ph-TADDOL		235

^{*a*} These compounds were observed in a NMR experiment on mixing 1 equiv of NpF₄-Li with 1 equiv of PCl₃. ^{*b*} The CIP descriptor defines the phosphorus stereocenter; the diastereoisomers were separated by preparative HPLC.

example, is only around ca. 80 Hz,²¹ whereas the ${}^{1}J(P,F)$ value for PF₃ is 1400 Hz.²²

The measured J(P,F) coupling constants nicely reflect the s character of the phosphorus lone pair, which increases when electron-withdrawing substituents are introduced, according to Bent's rule.²² Thus, this parameter may be viewed as equivalent to ${}^{1}J(Se,P)$ for phosphine selenides used for the quantification of σ -donor properties of phosphorus ligands.^{24–28}

Since this type of coupling involves the phosphorus lone pair, the J(P,F) value should decrease upon coordination to a metal. We reacted phosphine 1 with $[Ir_2Cp^*_2Cl_2(\mu-Cl)_2]$, and indeed, J(P,F) decreased to only 8 Hz upon formation of complex **12** (Scheme 1, Figure 3). The resulting Ir(III) complex was then treated with a chloride scavenger (AgSbF₆ or AgBF₄) and J(P,F) increased again to 80 Hz, clearly indicating that the electron-deficient 16-electron complex **13** saturates its coordination sphere by interacting with the remote F¹ of the NpF₄ unit. The ¹⁹F and ³¹P NMR spectra corresponding to compounds **1**, **12**, and **13**, respectively, are shown in Figure 3.

It is easily recognized that the Ir(III) center is stereogenic in complex 13. Therefore, the two phenyl substituents on phosphorus are diastereotopic and should give rise to different sets of resonances in NMR spectra. However, as

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Figure 3. ³¹P and ¹⁹F NMR spectra corresponding to phosphine 1 (top) and the neutral as well as the monocationic Ir(III) complexes 12 (middle) and 13 (bottom), respectively, at 298 K in CD_2Cl_2 .

Scheme 1. Synthesis of an Ir(III) Complex with Phosphine 1 and Subsequent Chloride Abstraction Resulting in a CF···Ir Interaction



shown in Figure 3, the ¹⁹F and ³¹P resonances of compound 13 are rather broad, thus indicating a dynamic behavior at room temperature. When samples were cooled to 193 K, resolved signals for the two diastereotopic phenyl groups were detected and, at the same time, the ³¹P resonance became much sharper, showing a slightly larger coupling constant to F^1 of 87 Hz (Figure 4). These findings corroborate the assumption of a stable Ir–F bond at low temperature, however, being involved in a dynamic process corresponding to an epimerization of the Ir center at room temperature.

The same sequence of iridium(III) complex formation/ chloride abstraction was carried out with the BINOLderived chiral phosphepine ligand 10. The presence of a chiral BINOL backbone on phosphorus should lead to two



Figure 4. Low-temperature (193 K) ¹³C and ³¹P NMR spectra of complex 13. Diastereotopic ortho and meta C-Ph signals corroborate the Ir–F interaction.

diastereomeric complexes upon chloride abstraction. Indeed, two expected products were observed in a 1.7:1 ratio, showing again augmented J(P,F) coupling constants of 40 Hz (major) and 51 Hz (minor). Unfortunately, these products were accompanied by two minor, unidentified side products and could not be characterized properly (see the Supporting Information for further details).

We obtained X-ray-quality single crystals of complexes 12 and 13, and the corresponding crystal structures were determined. ORTEP views are shown in Figure 5. The $Ir-F^1$ distance of 2.956(2) Å in compound 13 is just below the 3.0 Å threshold for a third-row transition-metal-fluorine interaction. However, since the interaction is strongly supported by our NMR experiments and because of the significant configurational change occurring on going from complex 12 to derivative 13, there should be no doubt about the existence of a stable interaction between iridium and fluorine in this case.

Complexes 12 and 13 display a significantly different geometry around the respective Ir(III) centers. Whereas complex 12 is pseudo-tetrahedral, as expected, 13 is distorted trigonal pyramidal with the P, Cl, and Ir atoms and the Cp* centroid almost perfectly lying in one common plane, while the remote fluorine occupies the apical position of the pyramid. In fact, the distance of the Ir atom from the plane defined by the Cp* centroid and the P and Cl atoms is just 0.02 Å. Though this displacement is barely significant, it is interesting to note that it occurs toward the same side of the plane as the fluorine atom F^1 , whose distance from the plane is 2.666 Å. The observation of such a trigonal-pyramidal geometry led to the question whether common (pseudo) square-planar complexes could be expanded to squarepyramidal complexes with the remote fluorine atom occupying the apical position.

We therefore prepared chiral and nonchiral complexes of Pd(II) and Pt(II), respectively, as shown in Scheme 2.

All targeted complexes were obtained in fair to good yields. In the case where the chiral phosphepine ligand **10** was used, two different isomers were observed for each of the two metals, due to the two possible orientations of the allyl ligand with respect to the main coordination plane. Pleasingly, all six complexes showed clearly augmented J(P,F) coupling constants as shown in Table 2, again strongly supporting a metal-fluorine interaction. Furthermore, a coupling amounting to ca. 200 Hz between F¹ and ¹⁹⁵Pt was detected by the characteristic ¹⁹⁵Pt satellites in the ¹⁹F NMR spectrum of the Pt complexes. This lies at the lower limit of ¹J(Pt,F) values reported for Pt–F bonds in the range of 200–2000 Hz²⁹ but is

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Figure 5. ORTEP view (30% probability ellipsoids) of complex 12 (left) and the cation 13 (right). The Ir-F distance in 13 is 2.956(2) Å. Important differences between 12 and 13: the Ir-P distance increases from 2.3172(15) to 2.3523(10) Å; the F(1)-C(8) distance increases from 1.325(7) to 1.346(4) Å; the Ir-P-C(1) angle decreases from 115.53(19) to $113.66(11)^\circ$.

Scheme 2. Synthesis of Pseudo-Square-Planar Palladium and Platinum Complexes Containing Achiral or Chiral NpF₄ Ligands



ii) 0.5 eq. [PdCl(allyl)]₂, CH_2Cl_2 , rt.

still much higher than in complex **D**, shown in Figure 2, for which a J(Pt,F) value of 11.5 Hz was interpreted as indicating an interaction.¹⁵

In a 2D NMR ¹⁹⁵Pt–¹⁹F correlation experiment performed on complexes **14** and **16a,b** it was possible to directly detect the interactions of interest. The spectrum of complexes **16a,b** is depicted in Figure 6, the cross peaks between F¹ and Pt nicely confirming the interaction (the corresponding spectrum of complex **14** can be found in the Supporting Information, p S47). To the best of our knowledge, it appears that this spectrum represents the first published example of a direct correlation experiment involving ¹⁹⁵Pt and ¹⁹F, although similar experiments have been reported for NMR-active metals such as ¹⁰⁹Ag, ¹⁸³W, and ²⁰⁷Pb.³⁰

Although the metal-fluorine interaction is strongly supported by NMR spectroscopy, it was necessary to corroborate the results with geometric parameters of the corresponding derivatives in the solid state. We were able to obtain single crystals of the achiral complexes **14** and **15**, which were subjected to an X-ray crystal structure study (see the Supporting Information for full details). As expected, in these two compounds the NpF₄ unit points toward the metal center and the crucial distances Pt- F^1 for complex **14** and Pd- F^1 for **15** are 3.0690(17) and 2.995(2) Å, respectively. There have been no reports of

Table 2. Selected Coupling Constants Supporting a Metal– Fluorine Interaction in Complexes 14–17 (Measured at Room Temperature)

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$J(\mathbf{P},\mathbf{F})$ (Hz)	J(Pt,F) (Hz)	$^{1}J(\mathrm{Pt,P})$ (Hz)			
67	204	4551			
61	173	6498			
52	241	6423			
98					
96 ^a					
99^a					
	<i>J</i> (P,F) (Hz) 67 61 52 98 96 ^a 99 ^a	$\begin{array}{c c} J(P,F) (Hz) & J(Pt,F) (Hz) \\ \hline 67 & 204 \\ 61 & 173 \\ 52 & 241 \\ 98 \\ 96^a \\ 99^a \\ \hline \end{array}$			

^a Measured at 223 K.

nonfluorinated analogues of these compounds. However, a structurally somewhat related complex containing diphenyl-(1-naphthyl)phosphine is $[Pt(N_3)_2(SMe_2)PPh_2Np]$.³¹ In this compound the distance between Pt and the hydrogen atom attached to C(8) of the naphthyl unit, corresponding to F¹ in complex 14, is 3.37 Å: i.e., longer than the Pt-F distance in our example.

In order to obtain more data for comparison, four related d^8 square-planar complexes were prepared, i.e. the Rh(I) and Ir(I) complexes 18-21 (Scheme 3). The isolated yields of these compounds were rather low, due to their high solubility even in pentane, which was used for their precipitation from the reaction mixtures, as well as to their reactivity and hence lower stability. The chiral complexes 20 and 21 were not isolated as solids but only investigated in solution by NMR.

These related compounds showed a J(P,F) coupling constant in the expected range. The corresponding values are collected in Table 3.

Unfortunately, the Rh- F^1 coupling in **19** and **21** is not directly observable, this not being surprising, since it is known that ${}^1J(Rh,F)$ values lie around 50 Hz²⁹ and the coupling in this case is expected to be weaker than ${}^1J(Rh,F)$. Because F^1 also couples to other fluorine atoms of the NpF₄ group, the extent of the coupling being around 20 Hz, the interesting J(Rh,F) parameter becomes hardly discernible. In principle, a stable CF-metal bonding interaction should lead to two different diastereoisomers in the case of complexes **20** and **21**. However, in our cases only one isomer was detected below room temperature. This observation indicates a very weak metal-fluorine interaction, with the NpF₄ unit still freely rotating. These additional complications demanded the use of 2D NMR ${}^{103}Rh - {}^{19}F$ correlation spectroscopy for the unambiguous identification of the interaction. The correlation spectrum obtained for complex **21** is shown in Figure 7.

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Figure 6. ¹⁹⁵Pt, ¹⁹F correlation spectrum of diastereomeric complexes 16, indicating the Pt-F interaction.



Table 3. Selected Coupling Constants for Complexes 18-21

complex	$J(\mathbf{P},\mathbf{F})$ (Hz)	J(Rh,F) (Hz)	$^{1}J(Rh,P)$ (Hz)
18	62		
19	75	n.d.	150
20	50		
21	66	< 10	234

Although J(Rh,F) is not directly observable in 1D NMR spectra, the cross peaks in the 2D correlation spectrum directly identify the Rh-F interaction in complex **21**. Since the J(P,F) values for the iridium analogues are also strongly increased, we assume a similar metal-fluorine interaction in the iridium(I) complexes **18** and **20**. To substantiate this assumption, single crystals of compounds **18** and **19** were analyzed by X-ray diffraction. The corresponding ORTEP views are shown in Figure 8.

The metal-fluorine distances in these cases lie above the threshold of 3.0 Å set by Plenio.³ However, since the interaction has been identified by means of 2D NMR techniques and a fairly large J(P,F) coupling constant has been detected, it may be necessary to relativize the simple distance



Figure 7. HMQC ¹⁰³Rh, ¹⁹F correlation spectrum of complex 21.

criterion and put it into a broader perspective. It is clear that for any other metal center its formal oxidation state, its ligand environment, and its possible geometrical constraints will change its ability to undergo such an interaction. Our analysis of complexes **18** and **19** indicates that such an interaction is operative, albeit rather weakly, at a M-Fdistance beyond 3.0 Å.

To enhance the interaction between the metal and the fluorine in the series of complexes 14-21, the obvious next step was the generation of coordinatively unsaturated species by chloride abstraction. Unfortunately, all experiments commonly using AgSbF₆ as scavenger resulted in complex and highly unstable product mixtures, from which no single product could be isolated. In some rare cases, though, it has been possible to detect species in solution



Figure 8. ORTEP view (30% probability ellipsoids) of complexes 18 and 19, respectively. Selected distances (Å): for 18, $Ir-F^1 =$ 3.0744(14), Ir-P = 2.3203(7), Ir-Cl = 2.3614(6); for 19, $Rh-F^1 =$ 3.0997(8), Rh-P = 2.3381(3), Rh-Cl = 2.3699(3).

displaying large *J*(P,F) coupling constants up to 150 Hz. However, the complex mixtures rapidly degraded, giving elemental metals within a few hours. Because of these difficulties, further investigations were abandoned. Similar considerations apply to the derivatives [RuCp*Cl₂-(PPh₂NpF₄)], [Ru(*p*-cymene)Cl₂(PPh₂NpF₄)], and [RhCp*Cl₂-(PPh₂NpF₄)].

The scope of transition metals was further extended to gold(I). In particular, the simple linear complexes [AuCl(1)] (22) and [AuCl(10)] (23) were prepared. In both cases, and by analogy to the previously discussed complexes, the observed J(P,F) coupling constants of 75 and 66 Hz, respectively, seem to indicate a M-F interaction. For complex 22, which was characterized by X-ray crystallography, the fluorine-gold distance is 3.1771(13) Å. This is in fact longer than the sum of the individual van der Waals radii of 3.13 Å, but we also assign this as remote, weak metal-fluorine interactions due to the increased J(P,F) coupling constants.

Conclusions

Utilizing the new phosphorus ligands 1 and 10, containing the 5,6,7,8-tetrafluoronaphthalen-1-yl fragment, a series of late-transition-metal complexes have been prepared and characterized by multinuclear NMR spectroscopy and X-ray crystal structural analyses, in view of identifying a possible bonding interaction of the fluorine atom at position 8 of the naphthyl group with the metal center. The main argument for claiming such an interaction is the relatively large J(P,F) coupling constant in the approximate range 40–100 Hz observed for most of the derivatives. The argument is mainly based on the comparison between the Ir(III) complex 13, for which the bonding interaction is further supported by stereochemical considerations, and its precursor 12, having a much lower J(P,F) coupling constant. However, the interaction of a metal center with the remote fluorine seems to be weaker for the d^8 and d^{10} centers Ir(I), Rh(I), Pd(II), Pt(II), and Au(I). Overall, the very nature of the observed interactions remains speculative and is probably not identical in all cases. In this respect, the difference between complex 13 and the examined d⁸ systems is reminiscent of the distinction adopted for interactions of CH units with coordinatively unsaturated transition-metal centers. Thus, remote CH-M interactions are divided into agostic (three-center-two-electron bonds) and anagostic (electrostatic) interactions.³² It is not surprising that there is no such discrimination known for remote CF-M interactions, because of the comparatively small selection of complexes displaying CF-M contacts and because of the general tendency of CF units to undergo electrostatic (i.e., "CF-anagostic") interactions. Thereby, such an electrostatic interaction could be seen as one between the metal and the fluorine atom or as a metal-dipole (CF) interaction, as already described by Takemura.⁸ Since not only the CF bond but also the whole NpF4 unit possesses significant dipole moments (2.83 D for 1-methyl-5,6,7,8-tetrafluoronaphthalene, as calculated by DFT B3LYP 6-31G*, and 1.83 D for the CF bond in fluoromethane³³), the alignment of the NpF₄ dipole antiparallel to the one of the Pd-P bonds may also be a strong stabilizing electrostatic effect. There are many examples of so-called "closed-shell interactions",³⁴ i.e. stabilizing interactions between d⁸-d¹⁰-s² systems. These interactions are generally weaker than covalent or ionic bonds but stronger than other van der Waals bonds. Whether or not the interaction of fluorine with Pd(II), Pt(II), Ir(I), Rh(I), and Au(I) could be interpreted as such a closed-shell interaction remains an open question. We are still pursuing the study of further organometallic systems possibly displaying these kinds of subtle interactions.

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Supporting Information Available: Text and figures giving full experimental details for the preparation of all new compounds described in this paper, including copies of ¹H, ¹⁹F, ³¹P and ¹³C NMR spectra, and CIF files giving crystallographic data and refinement parameters and bond lengths and angles of compounds **1**, **12–15**, **18**, **19**, and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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