Syntheses and Carbonyliridium Complexes of Unsymmetrically Substituted Fluorous Trialkylphosphanes: Precision Tuning of Electronic Properties, Including Insulation of the Perfluoroalkyl Groups

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Reactions of iodides $I(CH_2)_mR_{f8}$ [m = 2•4; $R_{f8} = (CF_2)_7CF_3$] and $LiPH_2 \cdot DME$ (•45 °C, THF) give the primary phosphanes $PH_2(CH_2)_mR_{f8}$ (**7**•**9**; 48•76%). Radical-initiated reactions (100 °C) of **7** and $H_2C{=}CHCH_2R_{f8}$, **8** and $H_2C{=}CHR_{f8}$ or $H_2C{=}CHCH_2CH_2R_{f8}$, and **9** and $H_2C{=}CHCH_2R_{f8}$, give the title phosphanes $P[(CH_2)_mR_{f8}]_2[(CH_2)_{m'}R_{f8}]$ [m/m' = 2/3 (**10**), 3/2 (**11**), 3/4 (**12**), 4/3 (**13**); 70•76%]. The symmetrically substituted phosphane $P[(CH_2)_mR_{f8}]_3$ (m = 5, **6**) is similarly prepared from PH_3 and $H_2C{=}CHCH_2CH_2CH_2R_{f8}$, analogously to previously reported homologs [m = 2 (**2**), 3 (**4**), 4 (**5**)]. Reactions of **10**•**13** and **2**, **4**, **5**, and **6** with $[Ir(COD)Cl]_2$ and CO give *trans*-$Ir(CO)(Cl)(PR_2R')_2$ (70•83%). The IR ν_{CO} values show a monotonic decrease with increasing numbers of CH_2 groups. Phosphanes **13**, **5**, and **6** have the most CH_2 groups, and give ν_{CO} values 10, 7, and 4 cm$^{•1}$ higher than the unfluorinated phosphane $P[(CH_2)_7CH_3]_3$. Hence, **6** provides nearly complete insulation of the iridium center from the electronegative perfluoroalkyl groups. Analogous rhodium derivatives of **4** and **5** are also described.

Introduction

The development of catalysts and reagents that have high affinities for "fluorous" phases has proceeded rapidly since Horváth described the concept and successful application of "fluorous biphase catalysis" in 1994.[1,2] This technique makes use of (1) the temperature-dependent miscibility of organic solvents with perfluorocarbons, perfluoroethers, or perfluoroamines,[3] and (2) "pony tails" of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$ [abbreviated $(CH_2)_mR_{fn}$], which when added to catalysts and reagents in sufficient numbers, provide exceptional degrees of fluorous-phase immobilization. Reactions can be conducted in mixtures of organic and fluorous solvents under monophasic conditions at higher temperatures, and the products (which normally have much greater affinities for the organic solvent) separated from the fluorous catalyst or reagent under biphasic conditions at lower temperatures. The recovered catalyst can then be reused, or the transformed reagent can, in some manner, be recycled.

Most of the fluorous metal catalysts developed to date feature fluorous phosphanes.[1,4,5] This has in turn required syntheses of new phosphanes, as well as methodologies that are practical on larger scales. Earlier we reported convenient multigram syntheses of the symmetrically substituted fluorous trialkylphosphanes **1**−**5** listed in Scheme 1 by free-radical chain additions of PH_3 to the corresponding alkenes $H_2C{=}CH(CH_2)_{m-2}R_{fn}$.[6] The related phosphane **6** is new to this work and described further below. Note that **1**, **2**, and **3** define a series with progressively longer R_{fn} groups, and that **2**, **4**, **5**, and **6** define a series with progressively longer $(CH_2)_m$ segments between an R_{f8} group and the phosphorus atom.

$$\begin{matrix} PH_3 \\ + \\ H_2C{=}CH(CH_2)_{m-2}R_{fn} \end{matrix} \xrightarrow[\begin{matrix}\text{2. } H_2C{=}CH(CH_2)_{m-2}R_{fn} \\ \text{VAZO, 90-100 °C}\end{matrix}]{\text{1. AIBN, 85 °C}} P((CH_2)_mR_{fn})_3$$

$$\boxed{R_{fn} = (CF_2)_{n-1}CF_3}$$

Phosphane	$(CH_2)_mR_{fn}$	Partition coefficient $CF_3C_6F_{11}$/toluene (27 °C)
1	$(CH_2)_2R_{f6}$	98.8 : 1.2
2	$(CH_2)_2R_{f8}$	>99.7 : <0.3
3	$(CH_2)_2R_{f10}$	>99.7 : <0.3
4	$(CH_2)_3R_{f8}$	98.8 : 1.2
5	$(CH_2)_4R_{f8}$	98.9 : 1.1
6	$(CH_2)_5R_{f8}$	98.9 : 1.1

Scheme 1. Syntheses and partition coefficients of symmetrically substituted fluorous trialkylphosphanes **1**−**6**

The phosphanes **1**−**6** exhibit a number of interesting trends. For example, all fluorous-phase affinities − as measured by the partition coefficients in Scheme 1 − are high. However, they become higher as the R_{fn} group is lengthened in **1**−**3**. They also appear to decrease as the $(CH_2)_m$ segment is lengthened in **2**, **4**, **5**, and **6**. As would be intuitively expected, air oxidations become progressively faster in this

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series. We sought to further fine tune these and other physical properties, and quantify the effect of the $(CH_2)_m$ segment length upon the phosphorus lone pair basicity.

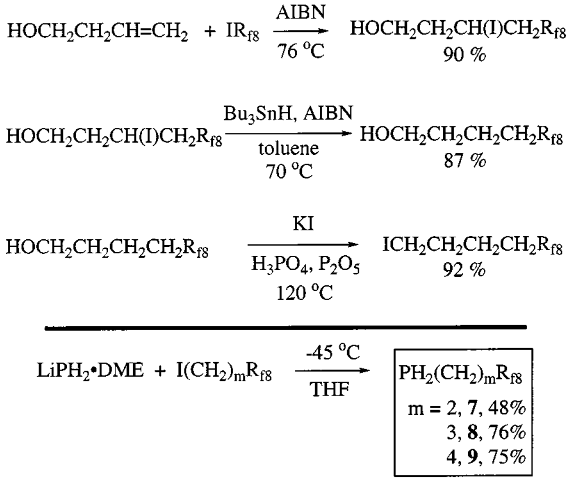
In this paper, we describe convenient syntheses of unsymmetrically substituted fluorous trialkylphosphanes of the formula $P[(CH_2)_mR_{f8}]_2[(CH_2)_{m'}R_{f8}]$. These feature mixtures of the types of pony tails in symmetrically substituted **2**, **4**, and **5**, and should thus have intermediate electronic characteristics. The unsymmetrical phosphanes are, together with **2**, **4**, **5**, and **6**, affixed to carbonylmetal fragments that provide IR assays of their donor/acceptor properties.[7] The most important results of this work are (1) a "toolkit" par excellence of nearly isosteric fluorous aliphatic phosphanes with precisely modulated electronic properties, and (2) the determination of the $(CH_2)_m$ segment lengths necessary to insulate the metal center from the electron-withdrawing R_{f8} groups.

Results

1. Phosphane Syntheses

We first sought convenient routes to the primary fluorous phosphanes $PH_2(CH_2)_mR_{f8}$ [m = 2 (**7**), 3 (**8**), 4 (**9**)]. These were anticipated to be versatile building blocks for many purposes, including free-radical additions to fluorous alkenes similar to those in Scheme 1. The strong nucleophile $LiPH_2 \cdot DME$ is easily prepared from PH_3 and *n*BuLi.[8] Hence, we set out to investigate alkylations, using the fluorous primary alkyl iodides $I(CH_2)_mR_{f8}$.

The iodide with two methylene groups, $I(CH_2)_2R_{f8}$, is commercially available. The next higher homolog, $I(CH_2)_3R_{f8}$, was prepared from the commercially available fluorous alcohol $HOCH_2CH_2CH_2R_{f8}$ and KI in an H_3PO_4/P_2O_5 slurry at 120 °C. A similar procedure has been communicated by another group.[9] The next higher homolog, $I(CH_2)_4R_{f8}$, has been reported only in patents.[10] It was synthesized on a 40-g scale in three steps as shown in Scheme 2 (top). First, the commercially available homoallylic alcohol $HOCH_2CH_2CH{=}CH_2$ and IR_{f8} were treated neat with a radical initiator to give $HOCH_2CH_2CH(I)CH_2R_{f8}$ in 90% yield after crystallization. Treatment with Bu_3SnH and a radical initiator gave the deiodinated alcohol $HOCH_2CH_2CH_2CH_2R_{f8}$ in 87% yield after crystallization. Related procedures for these two steps have been independently reported.[11] Subsequent reaction with KI in an H_3PO_4/P_2O_5 slurry at 120 °C gave analytically pure iodide in 92% yield after distillation.

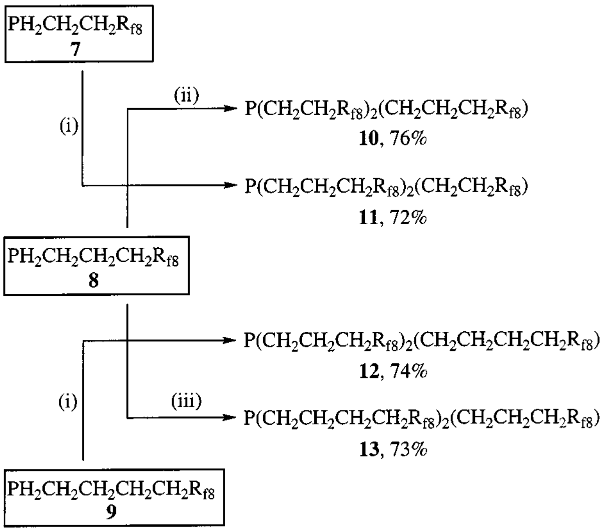


Scheme 2. Syntheses of building blocks for unsymmetrically substituted trialkylphosphanes

As depicted in Scheme 2 (bottom), $LiPH_2 \cdot DME$ and the fluorous iodides reacted in THF at −45 °C. Vacuum distillations gave the primary phosphanes **7** and **8** as clear liquids, and **9** as a low-melting white solid. The yield of **7** was slightly lower (49% vs. 75−76%), and some of the elimination product $H_2C{=}CHR_{f8}$ was detected in lower boiling fractions. A correct microanalysis was obtained for **9**, but not **7** and **8**. Accordingly, the ^1H NMR spectra of **7** and **8** (but not the ^{31}P NMR spectra) showed traces of impurities. The ^{31}P NMR spectra of **7**−**9** exhibited triplets diagnostic of two phosphorus-bound protons ($^1J_{PH}$ = 192−189 Hz; δ = −136.6 to −139.6, [D$_8$]THF), with much smaller longer-range couplings ($^2J_{PH}$ = 5−8 Hz) sometimes resolved. The ^1H NMR spectra showed PH_2 signals with the corresponding phosphorus coupling (dm, δ = 2.76−2.64, [D$_8$]THF).

The primary phosphanes **7**−**9** and slight excesses of the fluorous alkenes $H_2C{=}CH(CH_2)_{m-2}R_{f8}$ (m = 2−4;[6] 2.1−3.6 equiv.) reacted *neat* at 100 °C in the presence of a radical initiator (VAZO,[12] 5−6 mol-%). The combinations employed are illustrated in Scheme 3. The unsymmetrically substituted trialkylphosphanes $P[(CH_2)_mR_{f8}]_2[(CH_2)_{m'}R_{f8}]$ (**10**−**13**) were isolated as white powders in 76−72% yields (based upon **7**−**9**) after crystallization. They melted without decomposition between 49 and 69 °C, and were characterized by NMR spectroscopy and microanalysis, as described in the Experimental Section. The ^{31}P NMR signals of **10**−**13** (δ = −28.2, −31.3, −34.2, −33.6) were far downfield from those of **7**−**9**, as commonly seen for related tertiary and primary phosphanes. The $^1J_{CP}$, $^2J_{CP}$ and $^3J_{CP}$ values of **10**−**13** were of similar magnitude (17−15, 22−15 and 15−12 Hz), and always greater than those of **7**−**9** (e.g., $^1J_{CP}$ = 8−12 Hz). However, there were no obvious monotonic NMR-spectroscopic trends.

In the course of characterizing adducts of **12** and **13**, it became obvious that the inductive effect of the R_{f8} group was still being felt at the phosphorus atom. Hence, we sought the symmetrical phosphane with a five-methylene segment in every pony tail, $P[(CH_2)_5R_{f8}]_3$ (**6**). In order to apply the route in Scheme 1, the appropriate alkene was required. In previous work, we had shown that the iodides IR_{f8} and ICH_2R_{f8} were allylated by allyltri(*n*-butyl)stannane under free-radical chain conditions.[6] Thus, an analogous reaction was conducted with $I(CH_2)_2R_{f8}$, as shown in Equation (1). Workup gave the fluorous alkene $H_2C{=}CHCH_2CH_2CH_2R_{f8}$ in 52% yield after distillation (11-g scale). This compound has also been prepared by a related metal-catalyzed allylation.[13] Subsequent reaction with PH_3 (Scheme 1) gave **6** in 40% yield. Phosphane **6** was in general



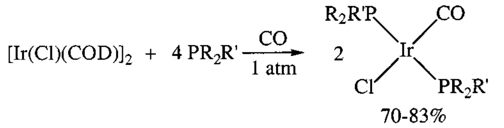
Scheme 3. Syntheses of unsymmetrically substituted fluorous trialkylphosphanes 10−13 at 100 °C with VAZO (initiator) and i) $H_2C{=}CHCH_2R_{f8}$, ii) $H_2C{=}CHR_{f8}$, iii) $H_2C{=}CHCH_2CH_2R_{f8}$

much less soluble than the lower homolog **5**. It dissolved in reasonable concentrations in the aromatic solvents toluene and $CF_3C_6H_5$, but was only sparingly soluble in perfluoro(methylcyclohexane), $CF_3C_6F_{11}$, the standard solvent for partition coefficients. Although **6** was always handled in a glove box, it would be expected to be more air-sensitive than **5**.[6]

$$\mathrm{Bu_3SnCH_2CH{=}CH_2 + ICH_2CH_2R_{f8}} \xrightarrow[\mathrm{CF_3C_6H_5,\ reflux}]{\mathrm{VAZO}} \mathrm{H_2C{=}CH(CH_2)_3R_{f8}} \qquad (1)$$

2. Carbonylmetal Derivatives

We sought to probe the basicities of the preceding trialkylphosphanes. The IR ν_{CO} values of carbonylmetal complexes are sensitive measures of the donor/acceptor properties of the metal fragment and consequently the other ligands. As shown in Scheme 4, carbonyliridium compounds of the type *trans*-$Ir(CO)(Cl)(PR_2R')_2$ − analogs of Vaska's complex − are conveniently prepared by treating $[Ir(COD)Cl]_2$ with phosphanes and then carbon monoxide in appropriate stoichiometry.[14] We have previously synthesized such complexes of the R_{f6} phosphane **1** and tri-*n*-octylphosphane, $P[(CH_2)_7CH_3]_3$ (**14** and **23**, Scheme 4).[7] The latter phosphane contains the same number of carbon atoms as **1**, but no fluorine atoms. Hence, it is a good model for a fluorous trialkylphosphane where "complete insulation" of the phosphorus atom from the perfluoroalkyl groups has been achieved.



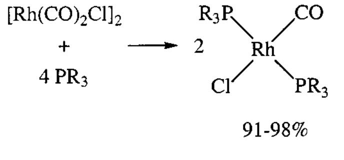
Complex	R	R'	IR $\tilde{\nu}_{CO}$ (cm^{-1})[a]	^{31}P NMR (δ)[b]
14	$(CH_2)_2R_{f6}$		1973.6[c]	18.2
15	$(CH_2)_2R_{f8}$		1973.9	17.5[d]
16	$(CH_2)_2R_{f8}$	$(CH_2)_3R_{f8}$	1965.2	15.5
17	$(CH_2)_3R_{f8}$	$(CH_2)_2R_{f8}$	1962.3	14.8
18	$(CH_2)_3R_{f8}$		1956.7	14.1
19	$(CH_2)_3R_{f8}$	$(CH_2)_4R_{f8}$	1954.8	13.5
20	$(CH_2)_4R_{f8}$	$(CH_2)_3R_{f8}$	1952.2	12.8
21	$(CH_2)_4R_{f8}$		1949.2	11.9
22	$(CH_2)_5R_{f8}$		1946.1	13.0[d]
23	$(CH_2)_7CH_3$		1942.3	14.0[e]

Scheme 4. Syntheses and key data for iridium complexes: [a] In $CF_3C_6H_5$, 10 mg/mL, spectrometer resolution ±0.5 cm^{-1}; [b] in $CF_3C_6F_{11}$ (unlocked; see Experimental Section); [c] this value was determined in $CF_3C_6H_5$ as part of this work (see also ref.[7]); [d] measured with a different spectrometer than the other compounds; [e] in C_6D_6 (insoluble in $CF_3C_6F_{11}$)

As summarized in Scheme 4, this procedure was repeated with the phosphanes **2** and **4−6** (Scheme 1), and **10−13** (Scheme 3). The corresponding iridium complexes **15−22** were isolated as analytically pure bright yellow powders in 70−83% yields. Adducts **15−21** were soluble in $CF_3C_6F_{11}$ and $CF_3C_6F_5$, but **22** was (like the free phosphane) only very slightly soluble in the former. All were sparingly soluble in THF, and insoluble in CH_2Cl_2. They were characterized by IR and ^{31}P NMR spectroscopy, as summarized in Scheme 4, as well as ^{1}H and/or ^{13}C NMR spectroscopy (Experimental Section). The IR measurements were made under identical conditions, at a resolution of ± 0.5 cm^{-1}. Analogous iridium complexes of some chiral, menthyl-substituted fluorous phosphanes are described elsewhere.[15]

Complexes **15−22** exhibited several monotonic trends. The ^{31}P NMR signals moved steadily upfield, except for **22** which was prepared and characterized in our new laboratories in Germany. There was also a progressive increase in air sensitivities in solution. Vaska-type complexes readily form η^2-O_2 adducts,[7] and the trend is consistent with increasing electron density on the iridium atom. As solids, several complexes oxidized more rapidly than the nonfluorinated species **23**, although the reverse order has been quantified in solution.[7] Finally, the IR ν_{CO} values steadily shifted to lower wavenumbers, nearly reaching that of nonfluorinated **23**. This important trend is also in agreement with increasing electron density on the iridium atom, but further analysis is deferred to the Discussion section.

A rhodium analog of the preceding complexes, *trans*-$Rh(CO)(Cl)[P[(CH_2)_2R_{f6}]_3]_2$ (**24**),[7,16] has been previously synthesized as shown in Scheme 5. Similar reactions of $[Rh(CO)_2Cl]_2$ with phosphanes **4** and **5** gave the higher homologs **25** and **26** as yellow prisms in 93−91% yields after recrystallization. The IR ν_{CO} values and ^{31}P NMR chemical shifts of **24**−**26** showed trends parallel to the iridium complexes (Scheme 5). The crystal structure of **24** was determined earlier.[7,16] X-ray data were also collected with **25**, using a CCD detector. However, the crystals were soft, the quality of the data set was poor, and refinement was thwarted by too much disorder near the ends of the pony tails. Extensive attempts were made to obtain crystals of other complexes in this study suitable for X-ray diffraction. Unfortunately, all efforts were unsuccessful.



Complex	R	IR $\tilde{\nu}_{CO}$ (cm^{-1})	^{31}P NMR (δ)
24	$(CH_2)_2R_{f6}$	1977[a]	23.5[b]
25	$(CH_2)_3R_{f8}$	1974[c]	19.2[d]
26	$(CH_2)_4R_{f8}$	1964[c]	17.5[d]

Scheme 5. Syntheses and key data for rhodium complexes: [a] In $CF_3C_6F_{11}$, from ref.[7]; [b] in [D$_6$]acetone (d, $^1J_{RhP}$ = 120 Hz), from ref.[7]; [c] in THF; [d] in [D$_8$]THF (d, $^1J_{RhP}$ = 117 Hz)

Discussion

The IR data for iridium complexes **14**−**23** in Scheme 4 and rhodium complexes **24**−**26** in Scheme 5 indicate a progressive increase in backbonding from the metal center to the carbonyl ligand. This in turn reflects the donor/acceptor properties of the phosphane ligands, and requires progressively increasing σ basicities, possibly augmented by very slightly diminishing π acidities. This conclusion is supported by collaborative photoelectron spectroscopy and calorimetric studies in progress,[17] as well as ongoing and earlier[1b] computational studies discussed below.

The IR data further show that the electronic properties of fluorous trialkylphosphanes can be precisely modulated by varying the lengths of the $(CH_2)_m$ segments. This can be done in concert, or by the new methodologies in Schemes 2 and 3, one pony tail at a time. Since the lengths of the $(CH_2)_m$ segments in a given phosphane do not differ by more than one (m/m' values), analyses can be cast in terms of the total number of methylene groups per phosphane − a quantity that varies from six (**1**, **2**) to fifteen (**6**). Complexes **14** and **15** also provide analytical reference points. Their nearly identical ν_{CO} values establish that the length of the perfluoroalkyl group can be neglected when it is six carbon atoms or longer.

Complexes **15**, **18**, **21**, and **22** feature symmetrically substituted phosphanes with six, nine, twelve, and fifteen methylene groups, respectively. The successive $\Delta\nu_{CO}$ increments (17.2, 7.5, 3.1 cm^{-1}) provide one basis for extrapolating to phosphanes with longer $(CH_2)_m$ segments. These represent 44−41% (7.5/17.2, 3.1/7.5) "transmission levels" per each increment of three methylene groups. As illustrated in Figure 1, this suggests ν_{CO} values of 1944.8, 1944.2, and 1943.9 cm^{-1} for the next three higher phosphanes $P[(CH_2)_mR_{f8}]_3$ (m = 6, 7, 8), and a limit of 1943.7 cm^{-1} for an infinite number of methylene groups. This is only slightly above the value for the nonfluorinated complex, **23** (1942.3 cm^{-1}). Thus, the phosphane **6** can be said to provide "nearly complete" insulation of the perfluoroalkyl groups from the iridium atom, the locus of the observed parameter. However, very slight improvements can be anticipated with additional methylene groups.

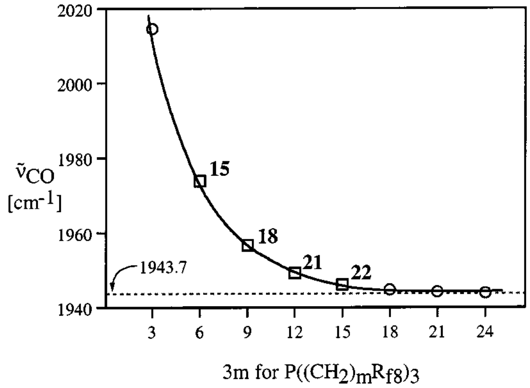


Figure 1. Relationship between IR ν_{CO} values of **15**, **18**, **21**, and **22**, and the total number of methylene groups in each phosphane ligand (□), and extrapolated values for homologous complexes (O)

Complexes **15**−**21** feature phosphanes in which the number of methylene groups increase from six to twelve. Here, the IR data illustrate the fine modulation of electronic properties. The largest $\Delta\nu_{CO}$ increments are 8.7 cm^{-1} (**15** vs. **16**) and 5.6 cm^{-1} (**17** vs. **18**). The others are in the range of 3.0−1.6 cm^{-1}. Although further arithmetic relationships can be noted, a particularly informative overview of all IR data is provided by Figure 2. In principle, any observable quantity that is a function of the number of repeat units x can be plotted versus $1/x$. Extrapolation to the y intercept ($1/x$ = 0) predicts a value for an infinite number of repeat units. The plot in Figure 2 is linear ($r^2 > 0.99$), and suggests a limit distinctly lower than that of the nonfluorinated complex **23**. However, we presently have greater confidence in the limiting value calculated from Figure 1.

There is the reciprocal question of the opposite limit − the ν_{CO} value of an analogous iridium complex of a tris(perfluoroalkyl)phosphane, $P(R_{fn})_3$. We are not aware of any such compounds in the literature. However, tris(pentafluorophenyl)phosphane, $P(C_6F_5)_3$, gives a value of 1994 cm^{-1}.[18] Extrapolation of Figure 1, as described above, gives 2014.5 and 2109.7 cm^{-1} for the iridium complexes of $P(CH_2R_{f8})_3$ and $P(R_{f8})_3$. The former is in reasonable agreement with that expected from an extrapolation of Figure 2 [2019.2 cm^{-1}; $1/(2m + m')$ = 0.333], but such plots are not reliable for lower numbers of repeat units.

Returning to the most highly insulated complex **22**, note that the inductive effect of the perfluoroalkyl groups is transmitted through seven atoms − five methylene carbon atoms, a phosphorus, and an iridium atom. To be fair, three

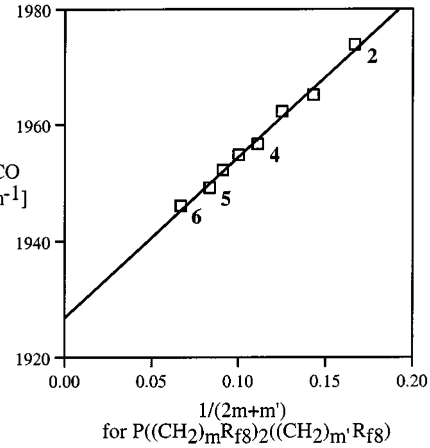


Figure 2. Relationship between IR ν_{CO} values of **15**−**22**, and the reciprocal of the total number of methylene groups in each phosphane ligand; selected ligands are designated by numbers for reference

pony tails converge at each phosphorus atom, and two phosphane ligands at the iridium atom. Normalization makes the data less dramatic. Nonetheless, to the best of our knowledge this represents the longest transmission of the inductive effect of a perfluoroalkyl group through a sequence of sp^3 atoms experimentally documented to date. Earlier, the pK_a values of amino acids $HO_2CCH(NH_2)(CH_2)_mCH_3$ and the ω-trifluoromethyl analogs $HO_2CCH(NH_2)(CH_2)_mCF_3$ were compared.[19] A measurable influence persisted through four sp^3 carbon atoms ($m = 3$).

We expect that the effect of the perfluoroalkyl groups in **1**−**6** and **10**−**13** will be more strongly felt when the locus of the observed parameter is the phosphorus atom (e.g., oxidation or ionization potential), and further studies are in progress.[17] We have characterized related fluorous trialkylamines $N[(CH_2)_mR_{f8}]_3$, and find a detectable influence upon basicities with five methylene groups.[20] At present, we have no evidence for "non-classical" transmission mechanisms (e.g., non-through-bond or non-field). However, in view of the tendency of fluorous groups to segregate − both intra- and intermolecularly − the possibility of a minor contribution remains an open question.

A computational study of the model fluorous trialkylphosphanes $P[(CH_2)_mCF_2CF_3]_3$ has been reported.[1b] The methylene chain lengths m were varied from zero to five. Both the phosphorus lone pair energies and the protonation energies reached asymptotic limits at five methylene groups (−9.2, −8.9 eV). However, they remained lower than those of the nonfluorinated reference compound $P[(CH_2)_3CH_3]_3$ (−8.7, −9.3 eV). Calorimetric data suggest that phosphane **1** is electronically similar to PMe_2Ph.[21] The latter gives an iridium complex with an IR ν_{CO} value of 1960 cm^{-1} (Nujol),[22] somewhat closer to those of phosphanes **4** and **11** (complexes **18**, **17**). However, in view of the different steric properties and measurement conditions, we regard this as a good agreement.

Phosphanes of the types **1**−**6** and **10**−**13** are very effective at immobilizing metal catalysts. For example, the tris(phosphane)rhodium complexes $Rh(Cl)[P[(CH_2)_2R_{fn}]_3]$ give partition coefficients of 693:1 to 811:1 (n = 6, 8), and exhibit very low leaching levels when used for alkene hydroboration (e.g., 4.5−2.2 ppm rhodium/mol product).[4b] Related rhodium hydroformylation catalysts behave similarly.[1b] The bis(phosphane) iridium complexes **15**−**23** should have somewhat lower partition coefficients, but still at useful levels (**14**: ca. 333:1 or 99.7:0.3 by NMR spectroscopy).[7] Importantly, phosphanemetal catalysts are commonly optimized by extensive variation of the ligand. Thus, **1**−**6** and **10**−**13** provide an exceptional "tool kit" for the precise electronic tuning of tri-*n*-alkylphosphane based catalysts, irrespective of any recovery objective.

One of several obvious future directions for fluorous phosphane synthesis would involve extensions to secondary or tertiary alkyl-substituted systems. Bulky phosphorus substituents are a key design element in many catalysts of current interest,[23] and these would sterically complement the phosphanes described above. With regard to this objective and others, the primary phosphanes **7**−**9** constitute very attractive building blocks. Although the precursor $LiPH_2$ must be prepared from PH_3, one atmosphere is sufficient − in contrast to the autoclave conditions required for the symmetrical trialkylphosphanes **1**−**6** in Scheme 1.

In summary, this study has provided a series of nearly isosteric fluorous trialkylphosphanes with finely modulated electronic properties. The inductive effects of the perfluoroalkyl groups are almost completely insulated from the phosphorus atom in **6**, which features five methylene groups per pony tail. Future reports will describe additional characterization of the electronic properties of these ligands,[17] as well as related fluorous amines,[20] new types of fluorous phosphanes, and their applications in catalysis.

Experimental Section

General: All reactions and workups involving phosphanes were conducted under inert gases. Commercial chemicals were treated as follows: $CF_3C_6F_{11}$, $CF_3C_6H_5$, distilled from P_2O_5; THF, hexane, heptane, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2; C_6D_6, $CDCl_3$, [D$_8$]THF (Cambridge Isotope), IR_{f8}, $ICH_2CH_2R_{f8}$, $HOCH_2CH_2CH_2R_{f8}$, $H_2C{=}CHR_{f8}$ (Oakwood), $HOCH_2CH_2CH{=}CH_2$, $Bu_3SnCH_2CH{=}CH_2$, Bu_3SnH, AIBN, VAZO (Aldrich), $[Ir(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$ (Strem), used as received; silica gel (Merck, grade 9385, 230−400 mesh), dried at 180 °C and $3\cdot10^{-3}$ Torr (24 h). − IR spectra were recorded with a Mattson Polaris spectrometer (0.5 cm^{-1} resolution). − NMR spectra were recorded with Varian or Jeol FT spectrometers at ambient probe temperature and referenced as follows: ^1H (300 MHz), external/residual C_6D_5H (δ = 7.16; external C_6D_6 lock for spectra in $CF_3C_6F_{11}$), residual [D$_7$]THF (δ = 3.58), residual [D$_5$]acetone (δ = 2.04), or residual $CHCl_3$ (δ = 7.27); ^{13}C (126 MHz), external C_6D_6 (δ = 128.39; lock for spectra in $CF_3C_6F_{11}$), internal [D$_8$]THF (δ = 67.57), or internal $CDCl_3$ (δ = 77.23); ^{31}P (121 MHz), external 85% H_3PO_4 (δ = 0.00); ^{19}F (282 MHz), external $CFCl_3$ (δ = 0.00). − Elemental analyses were conducted with a Carlo Erba EA1110 instrument (in-house, Erlangen), or by Atlantic Microlab (Norcross, Georgia).

$HOCH_2CH_2CH(I)CH_2R_{f8}$:[11a] A flask was charged with IR_{f8} (52.864 g, 96.826 mmol) and $HOCH_2CH_2CH{=}CH_2$ (8.456 g, 117.3 mmol). The solution was degassed (3 × freeze-pump-thaw) and AIBN (0.791 g, 4.82 mmol, 5 mol-%) was added. The mixture was heated at 76 °C. After 2 h, more AIBN (0.841 g, 5.12 mmol, 5 mol-%) was added. After 3 h, the solid mass was extracted with hot hexane (800 mL) and poured through filter paper. The filtrate was allowed to cool, and the resulting white crystals were collected on a frit. The filtrate was concentrated (100 mL), refluxed, and again cooled. A second crop of crystals was similarly collected. The filtrate was concentrated (20 mL), and a third crop similarly obtained. The crops were combined and dried by oil pump vacuum to give $HOCH_2CH_2CH(I)CH_2(CF_2)_7CF_3$ (53.578 g, 86.685 mmol, 90%), m.p. 82−83 °C (ref.[11a] 83 °C). − ^1H NMR ($CDCl_3$): δ = 4.56−4.47 (m, 1 H, C*HI*), 3.91−3.73 (m, 2 H), 3.07−2.75 (m, 2 H), 2.10−1.94 (m, 2 H), 1.46 (br s, 1 H, *H*O). − ^{19}F NMR ($CDCl_3$): δ = −81.3 (t, $^3J_{FF}$ = 9.2 Hz, 3 F, C*F*$_3$), −111.8 (dm, $^2J_{FF}$ = 272 Hz, 1 F), −114.6 (dm, $^2J_{FF}$ = 272 Hz, 1 F), −122.1 (m, 2 F), −123.2 (m, 4 F), −124.1 (m, 2 F), −126.6 (m, 2 F), −122.4 (m, 2 F). − MS (EI); *m/z* (%): 618 (3) [M^+], 491 (100) [M^+ − I], 473 (32) [M^+ − I, − H_2O], 441 (32), 395 (5), 219 (1) [$CF_3(CF_2)_3{}^+$], 169 (4) [$CF_3(CF_2)_2{}^+$], 119 (6) [$CF_3CF_2{}^+$], 69 (1) [$CF_3{}^+$]. − $C_{12}H_8F_{17}OI$ (618.06): calcd. C 23.32, H 1.30; found C 23.95, H 1.38.

$HOCH_2CH_2CH_2CH_2R_{f8}$:[11] A flask was charged with $HOCH_2CH_2CH(I)CH_2R_{f8}$ (52.495 g, 84.933 mmol), Bu_3SnH (49.968 g, 171.68 mmol), AIBN (1.426 g, 8.684 mmol, 10 mol-%) and toluene (200 mL). The solution was stirred at 70 °C. After 4 h, the solvent was removed by rotary evaporation. The residue was dissolved in hexane (50 mL) and cooled to −20 °C. The resulting white crystals were collected on a frit. The filtrate was concentrated (10 mL) and cooled to −20 °C. A second crop of crystals was similarly collected. The crops were combined and dried by oil pump vacuum to give $HOCH_2CH_2CH_2CH_2R_{f8}$ (36.200 g, 73.551 mmol, 87%). − ^1H NMR ($CDCl_3$):[11] δ = 3.68 (t, $^3J_{HH}$ = 6.0 Hz, 2 H, HOC*H*$_2$), 2.19−2.01 (m, 2 H, C*H*$_2$CF$_2$), 1.75−1.61 (m, 4 H, C*H*$_2$C*H*$_2$CH$_2$CF$_2$), 1.36 (br s, 1 H, *H*O). − ^{19}F NMR ($CDCl_3$): δ = −81.3 (t, $^3J_{FF}$ = 9.2 Hz, 3 F, CF_3), −115.0 (m, 2 F), −122.2 (m, 2 F), −123.2 (m, 4 F), −124.0 (m, 2 F), −126.6 (m, 2 F), −122.4 (m, 2 F).

$ICH_2CH_2CH_2CH_2R_{f8}$:[10] A flask was charged with P_2O_5 (64.284 g, 452.88 mmol), H_3PO_4 (85%, 125 mL, 2.17 mol), KI (31.346 g, 188.83 mmol), and $HOCH_2CH_2CH_2CH_2R_{f8}$ (35.128 g, 71.372 mmol), and fitted with a condenser. The mixture was stirred at 120 °C for 4 h, allowed to cool, and diluted with water (100 mL). The solution was extracted with ether (3 × 100 mL). The combined ether extracts were washed with aqueous $Na_2S_2O_3$ (100 mL, 0.1 M) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the residue distilled (100−110 °C ca. $1 \cdot 10^{-3}$ Torr) to give $ICH_2CH_2CH_2CH_2R_{f8}$ as a white solid (39.575 g, 65.731 mmol, 92%), m.p. 50−51 °C. − ^1H NMR ($CDCl_3$): δ = 3.21 (t, $^3J_{HH}$ = 7 Hz, 2 H, IC*H*$_2$), 2.21−2.00 (m, 2 H), 1.99−1.87 (m, 2 H), 1.82−1.70 (m, 2 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial): δ = 32.8 [s ($^1J_{CH}$ = 126 Hz),[25] one of *C*H$_2$*C*H$_2$CH$_2$CH$_2$CF$_2$], 30.1 [t, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 129 Hz),[25] *C*H$_2$CF$_2$], 21.6 [s ($^1J_{CH}$ = 129 Hz),[25] one of *C*H$_2$*C*H$_2$CH$_2$CF$_2$], 5.1 [s ($^1J_{CH}$ = 149 Hz),[25] I*C*H$_2$]. − ^{19}F NMR (δ, $CDCl_3$) −81.3 (t, $^3J_{FF}$ = 10 Hz, 3 F, C*F*$_3$), −114.8 (m, 2 F), −122.1 (m, 2 F), −122.3 (m, 4 F), −123.2 (m, 2 F), −123.9 (m, 2 F), −126.6 (m, 2 F). − MS (EI); *m/z* (%): 602 (10) [M^+], 475 (100) [M^+ − I], 455 (38) [M^+ − I, − HF]. − $C_{12}H_8F_{17}I$ (602.6): calcd. C 23.94, H 1.34; found C 23.87, H 1.28.

$PH_2CH_2CH_2R_{f8}$ (7): A Schlenk flask was charged with $ICH_2CH_2R_{f8}$ (8.958 g, 15.61 mmol) and THF (100 mL) and cooled to −45 °C (CH_3CN/N_2). Another Schlenk flask was charged with $LiPH_2 \cdot DME$ (2.020 g, 15.53 mmol)[8] and THF (50 mL). The second solution was added dropwise via cannula and with stirring to the first over a 30-min period. The cold bath was removed. After 2 h, the solvent was removed by oil pump vacuum, and $CF_3C_6H_5$ (20 mL) was added. The solution was filtered through a silica gel column (2 × 6 cm), which was rinsed with $CF_3C_6H_5$ (100 mL). The solvent was removed by oil pump vacuum, and the residue distilled (ca. 50−52 °C, 0.55 Torr) to give **7** as a colorless liquid (3.569 g, 7.434 mmol, 48%). − ^1H NMR ([D$_8$]THF): δ = 2.76 (dm, $^1J_{HP}$ = 192 Hz, 2 H, P*H*$_2$), 2.50−2.28 (m, 2 H, C*H*$_2$CF$_2$), 1.80−1.66 (m, 2 H, C*H*$_2$CH$_2$CF$_2$). − $^{13}C\{^1H\}$ NMR ([D$_8$]THF, partial): δ = 35.4 [dt, $^2J_{CP}$ = 2 Hz, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] *C*H$_2$CF$_2$], 5.6 [dt, $^1J_{CP}$ = 12 Hz, $^3J_{CF}$ = 4 Hz ($^1J_{CH}$ = 130 Hz),[25] *C*H$_2$CH$_2$CF$_2$]. − ^{19}F NMR ([D$_8$]THF): δ = −82.0 (t, $^3J_{FF}$ = 11 Hz, 3 F, C*F*$_3$), −115.8 (pseudoquint, J_{FF} = 17 Hz, 2 F), −122.6 (m, 6 F), −123.5 (m, 2 F), −124.2 (m, 2 F), −127.0 (m, 2 F). − ^{31}P NMR ([D$_8$]THF): δ = −136.6 (t of pseudoquint, $^1J_{PH}$ = 192 Hz, $^2J_{PH}$ = 8 Hz). − Analytical data see text.

$PH_2CH_2CH_2CH_2R_{f8}$ (8): The reaction and workup given for **7** was repeated with $ICH_2CH_2CH_2R_{f8}$ (9.697 g, 16.49 mmol)[9] and $LiPH_2 \cdot DME$ (2.151 g, 16.54 mmol).[8] Distillation (56−58 °C, 0.55 Torr) gave **8** as a colorless liquid (6.188 g, 12.52 mmol, 76%). − ^1H NMR ([D$_8$]THF): δ = 2.67 (dm, $^1J_{HP}$ = 190 Hz, 2 H, P*H*$_2$), 2.22 (tm, $^3J_{HF}$ = 19 Hz, 2 H, C*H*$_2$CF$_2$), 1.89−1.75 (m, 2 H), 1.67−1.53 (m, 2 H). − $^{13}C\{^1H\}$ NMR ([D$_8$]THF, partial): δ = 32.4 [dt, $^3J_{CP}$ = 5 Hz, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] *C*H$_2$CF$_2$], 25.1 [pseudoquadruplet, $^2J_{CP}$ = $^3J_{CF}$ = 4 Hz ($^1J_{CH}$ = 130 Hz),[25] *C*H$_2$CH$_2$CF$_2$], 14.2 [d, $^1J_{CP}$ = 10 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$]. − ^{19}F NMR ([D$_8$]THF): δ = −82.0 (t, $^3J_{FF}$ = 9 Hz, 3 F, C*F*$_3$), −115.0 (pseudoquint, J_{FF} = 15 Hz, 2 F), −122.6 (m, 6 F), −123.5 (m, 2 F), −124.2 (m, 2 F), −127.0 (m, 2 F). − ^{31}P NMR ([D$_8$]THF): δ = −139.6 (t of pseudoquint, $^1J_{PH}$ = 190 Hz, $^2J_{PH}$ = 5 Hz). − Analytical data see text.

$PH_2CH_2CH_2CH_2CH_2R_{f8}$ (9): The reaction and workup given for **7** was repeated with $ICH_2CH_2CH_2CH_2R_{f8}$ (9.426 g, 15.66 mmol) and $LiPH_2 \cdot DME$ (2.036 g, 15.66 mmol).[8] Distillation (70−73 °C, 0.55 Torr) gave **9** as a white solid (5.967 g, 11.74 mmol, 75%), m.p. near room temperature. − ^1H NMR ([D$_8$]THF): δ = 2.64 (dm, $^1J_{HP}$ = 189 Hz, 2 H, P*H*$_2$), 2.28−2.08 (m, 2 H, C*H*$_2$CF$_2$), 1.75−1.47 (m, 6 H). − $^{13}C\{^1H\}$ NMR ([D$_8$]THF, partial) δ = 33.6 [d, $^2J_{CP}$ = 4 Hz ($^1J_{CH}$ = 130 Hz),[25] PCH$_2$*C*H$_2$], 31.2 [t, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] *C*H$_2$CF$_2$], 22.2 [dt, $^3J_{CP}$ = 6 Hz, $^3J_{CF}$ = 4 Hz ($^1J_{CH}$ = 130 Hz),[25] *C*H$_2$CH$_2$CF$_2$], 14.2 [d, $^1J_{CP}$ = 9 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$]. − ^{19}F NMR ([D$_8$]THF): δ = −82.1 (t, $^3J_{FF}$ = 10 Hz, 3 F, CF_3), −115.2 (pseudoquint, J_{FF} = 15 Hz, 2 F), −122.7 (m, 6 F), −123.5 (m, 2 F), −124.3 (m, 2 F), −127.1 (m, 2 F). − ^{31}P NMR ([D$_8$]THF): δ = −139.6 (br t, $^1J_{PH}$ = 189 Hz). − $C_{12}H_{10}F_{17}P$ (508.2): calcd. C 28.36, H 1.98; found C 28.18, H 1.93.

$P(CH_2CH_2R_{f8})_2(CH_2CH_2CH_2R_{f8})$ (10): A culture tube was charged with **7** (1.013 g, 2.050 mmol), $H_2C{=}CHR_{f8}$ (3.309 g, 7.417 mmol) and VAZO (0.029 g, 0.12 mmol, 6.0 mol-%). The mixture heated at 100 °C for 12 h and cooled. $CF_3C_6H_5$ (20 mL) was then added, and the mixture was filtered through a silica gel column (2 × 6 cm). The column was rinsed with $CF_3C_6H_5$ (100 mL). The filtrates were concentrated by oil pump vacuum (20 mL) and cooled to 10 °C. A white powder formed, which was collected on a frit. The filtrate was concentrated (10 mL) and cooled to 10 °C. A second crop of white powder formed. The combined crops were dried by oil pump vacuum to give **10** (2.160 g, 1.558 mmol, 76%), m.p. 59.5−60.0 °C.

– ^{1}H NMR (CF$_3$C$_6$F$_{11}$): δ = 2.27–2.04 (m, 6 H), 1.86–1.71 (m, 2 H), 1.70–1.59 (m, 4 H), 1.52–1.43 (m, 2 H). – ^{13}C{^{1}H} NMR (CF$_3$C$_6$F$_{11}$, partial):[26] δ = 32.2 [td, $^3J_{CP}$ = 13 Hz, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$*C*H$_2$CF$_2$], 28.2 [pseudoquadruplet, $^2J_{CP}$ = $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] PCH$_2$*C*H$_2$CF$_2$], 26.9 [d, $^2J_{CP}$ = 15 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$*C*H$_2$CH$_2$CF$_2$], 17.1 [d, $^1J_{CP}$ = 17 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$CH$_2$CF$_2$],[24] 16.9 [d, $^1J_{CP}$ = 17 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$CH$_2$CH$_2$CF$_2$].[24] – ^{31}P NMR (CF$_3$C$_6$F$_{11}$): δ = –28.2 (s). – C$_{31}$H$_{14}$F$_{51}$P (1386.3): calcd. C 26.86, H 1.02; found C 26.50, H 1.00.

P(CH$_2$CH$_2$CH$_2$R$_{f8}$)$_2$(CH$_2$CH$_2$R$_{f8}$) (11): The reaction and workup given for **10** was repeated with **7** (1.027 g, 2.139 mmol), H$_2$C=CHCH$_2$R$_{f8}$ (2.832 g, 6.155 mmol)[6] and VAZO (0.027 g, 0.11 mmol, 5.0 mol-%). This gave **11** as a white powder (2.157 g, 1.540 mmol, 72%), m.p. 68.5–69.0 °C. – ^{1}H NMR (CF$_3$C$_6$F$_{11}$): δ = 2.26–2.00 (m, 6 H), 1.86–1.68 (m, 4 H), 1.68–1.55 (m, 2 H), 1.52–1.38 (m, 4 H). – ^{13}C{^{1}H} NMR (CF$_3$C$_6$F$_{11}$, partial):[26] δ = 32.3 [td, $^3J_{CP}$ = 13 Hz, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$*C*H$_2$CF$_2$], 28.3 [pseudoquadruplet, $^2J_{CP}$ = $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] PCH$_2$*C*H$_2$CF$_2$], 27.1 [d, $^2J_{CP}$ = 15 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$*C*H$_2$CH$_2$CF$_2$], 17.2 [d, $^1J_{CP}$ = 16 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$CH$_2$CF$_2$], 17.0 [d, $^1J_{CP}$ = 17 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$CH$_2$CH$_2$CF$_2$]. – ^{31}P NMR (CF$_3$C$_6$F$_{11}$): δ = –31.3 (s). – C$_{32}$H$_{16}$F$_{51}$P (1400.4): calcd. C 27.45, H 1.15; found C 27.35, H 1.11.

P(CH$_2$CH$_2$CH$_2$R$_{f8}$)$_2$(CH$_2$CH$_2$CH$_2$CH$_2$R$_{f8}$) (12): The reaction and workup given for **10** was repeated with **8** (1.106 g, 2.176 mmol), H$_2$C=CHCH$_2$R$_{f8}$ (3.032 g, 6.589 mmol)[6] and VAZO (0.033 g, 0.14 mmol, 6.0 mol-%). This gave **12** as a white powder (2.309 g, 1.616 mmol, 74%), m.p. 59.0–59.5 °C. – ^{1}H NMR (CF$_3$C$_6$F$_{11}$): δ = 2.23–1.92 (m, 6 H), 1.83–1.63 (m, 6 H), 1.58–1.45 (m, 2 H) 1.45–1.34 (6 H). – ^{13}C{^{1}H} NMR (CF$_3$C$_6$F$_{11}$, partial):[26] δ = 32.4 [td, $^3J_{CP}$ = 12 Hz, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$*C*H$_2$CF$_2$], 30.9 [t, $^2J_{CF}$ = 23 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$CH$_2$*C*H$_2$CF$_2$], 27.5 [d, $^2J_{CP}$ = 15 Hz ($^1J_{CH}$ = 130 Hz),[25] PCH$_2$*C*H$_2$CH$_2$CF$_2$],[24] 27.4, 25.8 [2 × d, J_{CP} = 15/15 Hz ($^1J_{CH}$ = 130/130 Hz),[25] PCH$_2$*C*H$_2$*C*H$_2$CH$_2$],[24] 21.9 [dm, $^3J_{CP}$ = 12 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$*C*H$_2$CH$_2$CF$_2$],[27] 17.1 [d, $^1J_{CP}$ = 17 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$CH$_2$CH$_2$CF$_2$]. – ^{31}P NMR (CF$_3$C$_6$F$_{11}$): δ = –34.2 (s). – C$_{34}$H$_{20}$F$_{51}$P (1428.4): calcd. C 28.59, H 1.41; found C 28.21, H 1.31.

P(CH$_2$CH$_2$CH$_2$CH$_2$R$_{f8}$)$_2$(CH$_2$CH$_2$CH$_2$R$_{f8}$) (13): The reaction and workup given for **10** was repeated with **7** (0.555 g, 1.12 mmol), H$_2$C=CHCH$_2$CH$_2$R$_{f8}$ (1.105 g, 2.330 mmol)[6] and VAZO (0.016 g, 0.065 mmol, 6.0 mol-%). This gave **13** as a white powder (1.183 g, 0.8201 mmol, 73%), m.p. 49.0–49.5 °C. – ^{1}H NMR (CF$_3$C$_6$F$_{11}$): δ = 2.23–1.91 (m, 6 H), 1.83–1.62 (m, 6 H), 1.58–1.44 (m, 4 H), 1.44–1.32 (m, 6 H); ^{13}C{^{1}H} NMR (CF$_3$C$_6$F$_{11}$, partial):[26] δ = 32.4 [td, $^3J_{CP}$ = 12 Hz, $^2J_{CF}$ = 22 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$*C*H$_2$CF$_2$], 30.9 [t, $^2J_{CF}$ = 23 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$CH$_2$*C*H$_2$CF$_2$], 27.62 [d, $^2J_{CP}$ = 15 Hz ($^1J_{CH}$ = 130 Hz),[25] PCH$_2$*C*H$_2$CH$_2$CF$_2$], 27.58, 25.9 [2 × d, J_{CP} = 15/16 Hz ($^1J_{CH}$ = 130/130 Hz),[25] PCH$_2$*C*H$_2$*C*H$_2$CH$_2$CF$_2$], 21.9 [dm, $^3J_{CP}$ = 12 Hz ($^1J_{CH}$ = 130 Hz),[25] CH$_2$CH$_2$*C*H$_2$CH$_2$CF$_2$],[27] 17.2 [d, $^1J_{CP}$ = 17 Hz ($^1J_{CH}$ = 130 Hz),[25] P*C*H$_2$CH$_2$CH$_2$CF$_2$]. – ^{31}P NMR (CF$_3$C$_6$F$_{11}$): δ = –33.6 (s). – C$_{35}$H$_{22}$F$_{51}$P (1442.4): calcd. C 29.14, H 1.54; found C 29.13, H 1.48.

H$_2$C=CHCH$_2$CH$_2$CH$_2$R$_{f8}$:[13] A Schlenk flask was charged with ICH$_2$CH$_2$R$_{f8}$ (25.000 g, 43.54 mmol), Bu$_3$SnCH$_2$CH=CH$_2$ (20.501 g, 61.91 mmol), VAZO (1.063 g, 4.35 mmol, 10 mol-%), and CF$_3$C$_6$H$_5$ (200 mL), and fitted with a condenser. The system was degassed (2 × freeze-pump-thaw) and refluxed. After 18 h, the solvent was removed by rotary evaporation (aerobic workup), and CH$_2$Cl$_2$ (200 mL) was added. The biphasic mixture was extracted with CF$_3$C$_6$F$_{11}$ (4 × 20 mL). The solvent was removed from the extracts by rotary evaporation. The residue was filtered through a silica gel column (2 × 10 cm), which was rinsed with CF$_3$C$_6$F$_{11}$ (100 mL). The solvent was removed from the filtrate by rotary evaporation and the residue distilled (62–64 °C, 3 mbar) to give H$_2$C=CHCH$_2$CH$_2$CH$_2$R$_{f8}$ as a colorless liquid (11.154 g, 22.85 mmol, 52%). – IR (neat or CHCl$_3$): $\nu_{C=C}$ = 1645 cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 5.82–5.70 (ddt, $^3J_{HH}$ = 17, 11, 7 Hz, 1 H, H$_2$C=C*H*), 5.09–5.02 (m, 2 H, *H$_2$*C=CH), 2.18–1.99 (m, 4 H), 1.76–1.68 (m, 2 H). – ^{13}C{^{1}H} NMR (CDCl$_3$, partial): δ = 136.9 (s, H$_2$C=*C*H), 116.3 (s, H$_2$*C*=CH), 32.9 (s, =CH*C*H$_2$), 30.2 (t, $^2J_{CF}$ = 22 Hz, *C*H$_2$CF$_2$), 19.4 (s, *C*H$_2$CH$_2$CF$_2$). – ^{19}F NMR (CDCl$_3$): δ = –81.0 (t, $^3J_{FF}$ = 10 Hz, 3 F, C*F$_3$*), –114.5 (pseudoquint, 2 F), –121.9 (m, 2 F), –122.2 (m, 4 F), –122.9 (m, 2 F), –123.7 (m, 2 F), –126.3 (m, 2 F). – MS (FAB); *m/z* (%): 487 (100) [M$^+$ – 1]. – C$_{13}$H$_9$F$_{17}$ (488.2): calcd. C 31.98, H 1.86; found C 32.12, H 1.79.

P(CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$R$_{f8}$)$_3$ (6): A bomb was charged with H$_2$C=CHCH$_2$CH$_2$CH$_2$R$_{f8}$ (3.089 g, 6.33 mmol), AIBN (0.103 g, 0.63 mmol, 10 mol-%), and PH$_3$ (15 bar). The bomb was partially immersed in an oil bath (85 °C), and the contents stirred. After 24 h, the bomb was vented, purged and opened. The yellow solid was dissolved in CF$_3$C$_6$H$_5$ (10 mL), and a ^{31}P NMR spectrum showed a mixture of phosphanes PH$_{3-n}$(CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$R$_{f8}$)$_n$ (*n* = 1/2/3 9:36:55; δ = –140.7, –70.4, –32.8). VAZO (0.500 g, 2.04 mmol) and H$_2$C=CHCH$_2$CH$_2$CH$_2$R$_{f8}$ (2.000 g, 4.10 mmol) were added. The mixture was stirred at 100 °C. After 12 h, the mixture was cooled and filtered through a silica gel column (2 × 6 cm), which was rinsed with CF$_3$C$_6$H$_5$ (60 mL). The solvent was removed from the filtrates by oil pump vacuum. CF$_3$C$_6$F$_{11}$ (10 mL) was added, and a white powder [by-product; ^{31}P{^{1}H} NMR spectroscopy (CF$_3$C$_6$H$_5$): δ = –5.9] was removed by filtration. The solvent was removed from the filtrate by oil pump vacuum. The residue was dissolved in CF$_3$C$_6$H$_5$ and cooled to –32 °C. A white powder formed, which was collected on a frit and dried by oil pump vacuum to give **6** (1.281 g, 0.85 mmol, 40% based upon initial alkene charge), m.p. 44.0 °C. – ^{1}H NMR (CF$_3$C$_6$F$_{11}$): δ = 2.02–1.86 (m, 6 H), 1.62–1.22 (m, 24 H). – ^{13}C{^{1}H} NMR (CDCl$_3$, partial): δ = 30.58 (t, $^2J_{CF}$ = 22 Hz, *C*H$_2$CF$_2$), 30.59 (d, *J* = 13 Hz, PCH$_2$CH$_2$*C*H$_2$), 19.8 (s, *C*H$_2$CH$_2$CF$_2$). – ^{31}P{^{1}H} NMR (CF$_3$C$_6$F$_{11}$): δ = –33.7 (s). – MS (FAB); *m/z* (%): 1515 (100) [M$^+$ + O], 1499 (45) [M$^+$]. – C$_{39}$H$_{30}$F$_{51}$P (1498.5): calcd. C 31.26, H 2.02; found C 31.50, H 2.36.

***trans*-Ir(CO)(Cl)[P(CH$_2$CH$_2$R$_{f8}$)$_3$]$_2$ (15):** A Schlenk flask was charged with [Ir(COD)Cl]$_2$ (0.0170 g, 0.0253 mmol), P(CH$_2$CH$_2$R$_{f8}$)$_3$ (**2**;[6] 0.140 g, 0.102 mmol) and CF$_3$C$_6$H$_5$ (7 mL). The solution was stirred for 20 min. The flask was momentarily evacuated and refilled with CO. After 1 h, the solution was concentrated by oil pump vacuum (ca. 2 mL), and hexane was added (10 mL). The yellow precipitate was collected on a frit and dried by oil pump vacuum to give **15** (0.110 g, 0.0366 mmol, 72%), m.p. 127.3–128.2 °C. – IR and ^{31}P NMR: Scheme 4. –^{1}H NMR (CF$_3$C$_6$F$_{11}$): δ = 2.92–2.52 (m, 24 H). – C$_{61}$H$_{24}$ClF$_{102}$IrOP$_2$ (3000.3): calcd. C 24.42, H 0.81; found C 24.30, H 0.81.

***trans*-Ir(CO)(Cl)[P(CH$_2$CH$_2$R$_{f8}$)$_2$(CH$_2$CH$_2$CH$_2$R$_{f8}$)]$_2$ (16):** The reaction and workup given for **15** was repeated with [Ir(COD)Cl]$_2$ (0.0310 g, 0.0462 mmol), **10** (0.265 g, 0.191 mmol) and CF$_3$C$_6$H$_5$ (15 mL). This gave **16** as a yellow powder (0.195 g, 0.0644 mmol, 70%), m.p. 111.5−112.0 °C. − IR and ^{31}P NMR: Scheme 4. − ^{1}H NMR ($CF_3C_6F_{11}$): δ = 2.62−1.92 (m, 28 H). − $C_{63}H_{28}ClF_{102}IrOP_2$ (3028.3): calcd. C 24.99, H 0.93; found C 24.52, H 0.92.

***trans*-Ir(CO)(Cl)$[P(CH_2CH_2CH_2R_{f8})_2(CH_2CH_2R_{f8})]_2$ (17):** The reaction and workup given for **15** was repeated with $[Ir(COD)Cl]_2$ (0.013 g, 0.019 mmol), **11** (0.111 g, 0.0793 mmol) and $CF_3C_6H_5$ (10 mL). This gave **17** as a yellow powder (0.085 g, 0.028 mmol, 72%), m.p. 72.5−73.0 °C dec. − IR and ^{31}P NMR: Scheme 4. − ^{1}H NMR ($CF_3C_6F_{11}$): δ = 2.64−1.88 (m, 32 H). − $C_{65}H_{32}ClF_{102}IrOP_2$ (3056.4): calcd. C 25.54, H 1.06; found C 25.63, H 1.16.

***trans*-Ir(CO)(Cl)$[P(CH_2CH_2CH_2R_{f8})_3]_2$ (18):** The reaction and workup given for **15** was repeated with $[Ir(COD)Cl]_2$ (0.0420 g, 0.0625 mmol), $P(CH_2CH_2CH_2R_{f8})_3$ (**4**;[6] 0.363 g, 0.257 mmol) and $CF_3C_6H_5$ (15 mL). This gave **18** as a yellow powder (0.290 g, 0.0940 mmol, 75%), m.p. 87.0−87.5 °C. − IR and ^{31}P NMR: Scheme 4. − ^{1}H NMR ($CF_3C_6F_{11}$): δ = 2.42−1.96 (m, 36 H). − $^{13}C\{^{1}H\}$ NMR ($CF_3C_6F_{11}$, partial): δ = 32.2 (tm, $^{2}J_{CF}$ = 22 Hz ($^{1}J_{CH}$ = 130 Hz),[25] $\mathit{C}H_2CF_2$), 24.6 (t, $^{3}J_{CF}$ = 16 Hz ($^{1}J_{CH}$ = 130 Hz),[25] $\mathit{C}H_2CH_2CF_2$), 16.2 (s ($^{1}J_{CH}$ = 130 Hz),[25] $P\mathit{C}H_2$). − $C_{67}H_{36}ClF_{102}IrOP_2$ (3084.4): calcd. C 26.09, H 1.18; found C 25.92, H 1.18.

***trans*-Ir(CO)(Cl)$[P(CH_2CH_2CH_2R_{f8})_2(CH_2CH_2CH_2CH_2R_{f8})]_2$ (19):** The reaction and workup given for **15** was repeated with $[Ir(COD)Cl]_2$ (0.0317 g, 0.0472 mmol), **12** (0.284 g, 0.199 mmol) and $CF_3C_6H_5$ (15 mL). This gave **19** as a yellow powder (0.227 g, 0.0729 mmol, 77%), m.p. 69.0−71.0 °C dec. − IR and ^{31}P NMR: Scheme 4. − ^{1}H NMR ($CF_3C_6F_{11}$): δ = 2.38−1.68 (m, 40 H). − $C_{69}H_{40}ClF_{102}IrOP_2$ (3112.5): calcd. C 26.63, H 1.30; found C 26.84, H 1.30.

***trans*-Ir(CO)(Cl)$[P(CH_2CH_2CH_2CH_2R_{f8})_2(CH_2CH_2CH_2R_{f8})]_2$ (20):** The reaction and workup given for **15** was repeated with $[Ir(COD)Cl]_2$ (0.0299 g, 0.0445 mmol), **13** (0.263 g, 0.182 mmol) and $CF_3C_6H_5$ (15 mL). This gave **20** as a yellow powder (0.2041 g, 0.06499 mmol, 73%), m.p. 82.5−83.5 °C dec. − IR and ^{31}P NMR: Scheme 4. − ^{1}H NMR ($CF_3C_6F_{11}$): δ = 2.38−1.68 (m, 44 H). − $C_{71}H_{44}ClF_{102}IrOP_2$ (3140.5): calcd. C 27.15, H 1.41; found C 27.15, H 1.42.

***trans*-Ir(CO)(Cl)$[P(CH_2CH_2CH_2CH_2R_{f8})_3]_2$ (21):** The reaction and workup given for **15** was repeated with $[Ir(COD)Cl]_2$ (0.0304 g, 0.0452 mmol), $P(CH_2CH_2CH_2CH_2R_{f8})_3$ (**5**,[6] 0.295 g, 0.202 mmol) and $CF_3C_6H_5$ (15 mL). This gave **21** as a yellow powder (0.212 g, 0.0669 mmol, 74%), m.p. 72.0−72.5 °C dec. − IR and ^{31}P NMR: Scheme 4. − ^{1}H NMR ($CF_3C_6F_{11}$): δ = 2.20−1.98 (m, 24 H), 1.92−1.70 (m, 24 H). − $^{13}C\{^{1}H\}$ NMR ($CF_3C_6F_{11}$, partial): δ = 30.7 [t, $^{2}J_{CF}$ = 23 Hz ($^{1}J_{CH}$ = 130 Hz),[25] $\mathit{C}H_2CF_2$], 24.9 [t, $^{3}J_{CF}$ = 16 Hz ($^{1}J_{CH}$ = 130 Hz),[25] $\mathit{C}H_2CH_2CF_2$], 24.4, 21.8 [2 × s ($^{1}J_{CH}$ = 130/130 Hz), $P\mathit{C}H_2\mathit{C}H_2$]. − $C_{73}H_{48}ClF_{102}IrOP_2$ (3168.6): calcd. C 27.67, H 1.53; found C 27.56, H 1.37.

***trans*-Ir(CO)(Cl)$[P(CH_2CH_2CH_2CH_2CH_2R_{f8})_3]_2$ (22):** A Schlenk flask was charged with $[Ir(COD)Cl]_2$ (0.0200 g, 0.030 mmol), **6** (0.1830 g, 0.122 mmol) and $CF_3C_6H_5$ (10 mL). The solution was stirred for 20 min. CO was bubbled through the orange solution for 10 min. After 1 h, the green solution was concentrated by oil pump vacuum (ca. 2 mL) and filtered through a silica gel column (2 × 2 cm), which was rinsed with $CF_3C_6H_5$ (10 mL). The filtrates were cooled to −32 °C. A yellow precipitate formed, which was collected on a frit and dried by oil pump vacuum to give **22** (0.1630 g, 0.050 mmol, 83%), m.p. 60.0−61.0 °C (capillary). − IR and ^{31}P NMR: Scheme 4. − ^{1}H NMR ($CF_3C_6F_{11}$): δ = 2.45−1.89 (m, 60 H). − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, partial): δ = 30.6 (t, $^{2}J_{CF}$ = 23 Hz, $\mathit{C}H_2CF_2$), 23.1 (m, $\mathit{C}H_2CH_2CF_2$), 20.3, 19.7, 19.4 (3 × s, $P\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2$). − MS (FAB); *m/z* (%): 3253 (100) [M^{+}]. − $C_{79}H_{60}ClF_{102}IrOP_2$ (3252.8): calcd. C 29.17, H 1.86; found C 29.55, H 1.98.

***trans*-Rh(CO)(Cl)$[P(CH_2CH_2CH_2R_{f8})_3]_2$ (25):** A Schlenk flask was charged with $[Rh(CO)_2Cl]_2$ (0.0071 g, 0.018 mmol), **4** (0.104 g, 0.0735 mmol) and $CF_3C_6H_5$ (10 mL). The solution was stirred for 1 h, and concentrated by oil pump vacuum (ca. 1 mL). CH_2Cl_2 was then added by vapor diffusion. After 48 h, the yellow prisms were collected by filtration and dried by oil pump vacuum to give **25** (0.100 g, 0.0334 mmol, 93%) m.p. 84.5−85.5 °C dec. − IR and ^{31}P NMR: Scheme 5. − ^{1}H NMR ([D$_8$]THF): δ = 2.50−2.20 (m, 12 H), 2.18−1.90 (m, 24 H). − $C_{67}H_{36}ClF_{102}OP_2Rh$ (2995.1): calcd. C 26.87, H 1.21; found C 26.59, H 1.25.

***trans*-Rh(CO)(Cl)$(P(CH_2CH_2CH_2CH_2R_{f8})_3)_2$ (26):** The reaction and workup given for **25** was repeated with $[Rh(CO)_2Cl]_2$ (0.0080 g, 0.020 mmol), **5** (0.120 g, 0.0824 mmol) and $CF_3C_6H_5$ (10 mL). This gave **26** as yellow prisms (0.118 g, 0.0383 mmol, 96%) m.p. 86.0−87.0 °C dec. − IR and ^{31}P NMR: Scheme 5. − ^{1}H NMR ([D$_8$]THF): δ = 2.50−1.60 (m, 48 H). − $C_{73}H_{48}ClF_{102}OP_2Rh$ (3079.3): calcd. C 28.47, H 1.57; found C 28.22, H 1.63.

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[24] Splitting patterns are partially coincidental; chemical shift and coupling constants deduced from visible peaks.

[25] Determined from a separate ^{13}C NMR spectrum (without ^{1}H decoupling).

[26] Assignments of resonances to the two like or one unique $(CH_2)_xR_{f8}$ segments were made on the basis of intensities.

[27] The multiplet appears to be a triplet (ca. 2 Hz), which would logically be assigned as a $^{3}J_{CF}$ coupling. Hence, this signal is provisionally assigned to the $PCH_2CH_2\mathit{C}H_2CH_2R_{f8}$ carbon atom.

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