

The Electrophilic Phosphinidene Complex ${}^i\text{Pr}_2\text{N}-\text{P}=\text{Fe}(\text{CO})_4$ Trapped by Alkynes

Jan B. M. Wit, Gerno T. van Eijkel, Marius Schakel and Koop Lammertsma*

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract—The in-situ formation at -30°C of the electrophilic phosphinidene complex ${}^i\text{Pr}_2\text{NPF}(\text{CO})_4$, resulting from reaction of dichlorophosphine ${}^i\text{Pr}_2\text{NPCl}_2$ with $\text{Na}_2\text{Fe}(\text{CO})_4$ (Collman's reagent), was demonstrated by trapping reactions with various alkynes. The resulting phosphirenes were obtained in good yields. The reactivity of ${}^i\text{Pr}_2\text{NPF}(\text{CO})_4$ is less than that of $\text{PhPW}(\text{CO})_5$, which is, however, generated at much higher temperatures. The stabilization of ${}^i\text{Pr}_2\text{NPF}(\text{CO})_4$ in the reaction medium is discussed. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Introduction

The chemistry of phosphinidenes has developed rapidly¹ since it was recognized in the early 1980s that the reactive carbene-like R–P species, which favor a triplet ground state even with highly electron-donating groups R, prefer a singlet state on metal complexation (R–P=ML_n).² This led to the synthesis of various stable nucleophilic phosphinidene complexes, some of which were characterized by X-ray crystal structure.³ In sharp contrast, terminal complexed electrophilic phosphinidenes have remained spectroscopically elusive. Using suitable precursors such as phosphanorbornadiene complexes,⁴ however, the transient species can be trapped with, e.g. olefins and alkynes to yield phosphiranes and phosphirenes, respectively.⁵

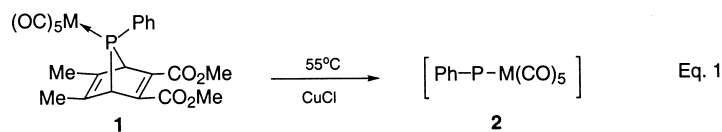
It is now well-recognized that the versatile and well-behaved chemistry of R–P=M(CO)₅ (M=W, Mo, Cr) **2** resembles that of the electrophilic carbenes.^{1a,6} Despite the many investigations into the properties of these reactive intermediates, the pathways by which the phosphinidenes can be generated remain limited. The most suitable route, developed by Mathey and coworkers,^{4,5} remains the cheletropic cleavage of complexed phosphanorbornadienes **1** (Eq. 1) (Scheme 1), but elimination of R–P=ML_n from other compounds has also been employed to a limited extent.⁷ In search of alternative pathways for generating electrophilic phosphinidene complexes we were interested in using more readily available phosphorus compounds, such as chlorophosphines. For introducing the transition

metal group the dianionic $\text{M}(\text{CO})_n^{2-}$ (M=Fe, Collman's reagent) seemed a reasonable candidate. Such a combination of reagents has, in fact, been used for the synthesis of both iron complexed diphosphenes⁸ and phosphorus/iron clusters.⁹ For example, King showed that reaction of dichlorophosphines R_2NPCl_2 (**4**) with $\text{Na}_2\text{Fe}(\text{CO})_4$ (**3**) can lead to an array of clusters (Eq. 2) (Scheme 2).^{9a} Interestingly, he suggested that the observed main product **9** results from initial formation of $\text{R}_2\text{N}-\text{P}=\text{Fe}(\text{CO})_4$ (**5**) followed by dimerization, rearrangement, and CO-loss via several routes.^{9a}

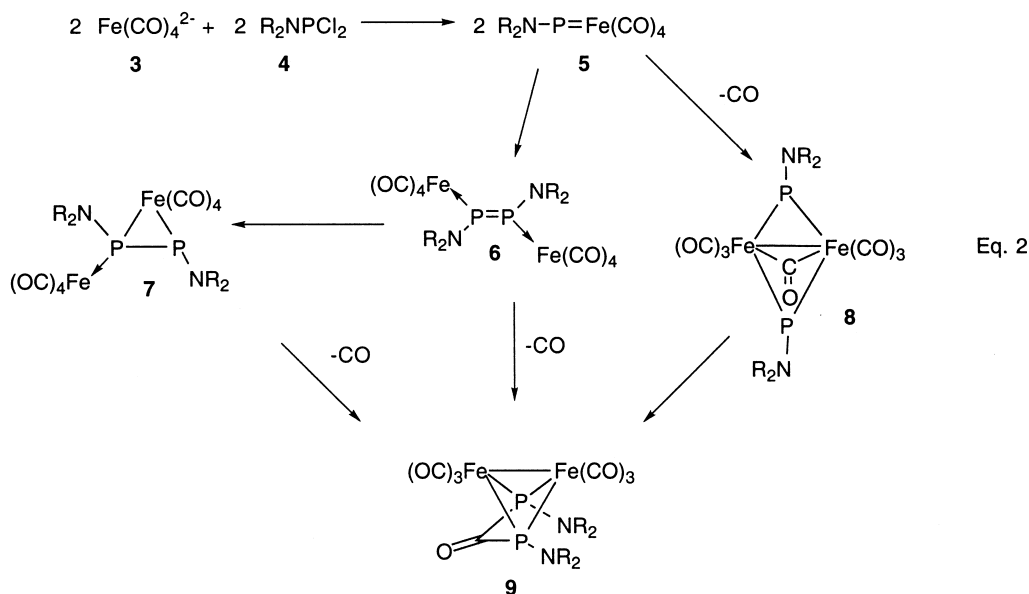
To our knowledge no attempts were made to identify **5** in a more direct manner, although Cowley has reported an X-ray structure of a related phosphinidene stabilized by a base $[\text{HB}(\text{pz}^*)_3]\text{PF}(\text{CO})_4$, $\text{pz}^*=\text{tris}(\text{pyrazolyl})\text{borate}$.¹⁰ The cluster composition (varying P/Fe ratios) in Eq. 2 appeared to be dependent on the solvent used (e.g. diethyl ether, hexanes or THF).^{9a} This may point to the limited solubility of Collman's reagent but also to substrate and/or solvent complexation of phosphinidene complex **5**, all of which are likely to influence the growth of the phosphorus/iron clusters. Moreover, dimerization of **5** to diphosphenes was reported as one of the routes that leads to the observed clusters. At first sight this is an unusual pathway because dimerization of carbenes is considered to be an unlikely process.¹¹ On the other hand, cheletropically generated R–P=W(CO)₅ does give W(CO)₅-complexed diphosphenes,¹² but their formation is likely to be more complicated than a simple dimerization as the presence of the 'extra' W(CO)₅ suggests (Eq. 3) (Scheme 3). Therefore, to establish whether indeed the condensation reaction between **3** and **4** generates 'free' **5** as a first product, we set out to trap this phosphinidene complex with alkynes.

Keywords: phosphinidene complex; Collman's reagent; phosphirenes.

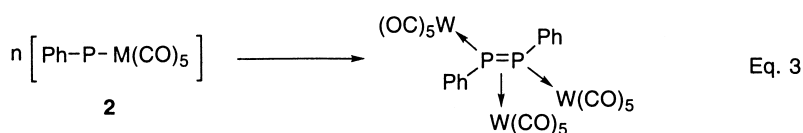
* Corresponding author. Tel.: +31-20-44474-74; fax: +31-20-4447488; e-mail: lammert@chem.vu.nl



Scheme 1.



Scheme 2.



Scheme 3.

Results and Discussion

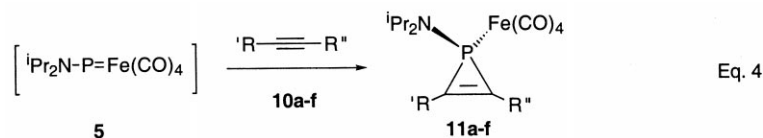
Reaction of dichloro(diisopropylamino)phosphine **4** with disodium tetracarbonylferrate **3** only, using diethyl ether as solvent, nicely reproduced King's earlier results,^{9a} which describe the formation of cluster **9** as the main product (see Eq. 2).

Next, the reaction of **3** with **4** was performed in the presence of various alkynes **10**, using pentane or diethyl ether as solvent, to give, as anticipated, the corresponding phosphirene complexes **11** (Eq. 4) (Scheme 4). The yields of these reactions are fair to good and are summarized in Table 1. The reagents **3**, **4**, and alkyne **10** were added in a 1:1:1 molar mixture to pentane or diethyl ether at -78°C and then

slowly heated from -30°C , where reaction starts as indicated by a color change, to room temperature for completion. The phosphirene complexes are easily handled without special conditions, but their stability increases substantially at lower temperatures.

The formation of the phosphirenes is strong support for the in situ generation of the electrophilic phosphinidene complex ${}^i\text{Pr}_2\text{N-P=Fe(CO)}_4$ (**5**) at ca. -30°C . Its expected high reactivity is confirmed by the high yield reactions with several alkynes (>80% isolated). We discuss some aspects of these reactions.

Addition of **5** to disubstituted alkynes occurs in high yield provided steric hindrance does not play a dominant role. The



Scheme 4.

Table 1. Phosphirene yields from the reaction of **5** with alkynes

Alkyne	Phosphirene	R'	R''	Yield (%)
2-Butyne (10a)	11a	CH ₃	CH ₃	52
Diphenylacetylene (10b)	11b	Ph	Ph	86
Phenylacetylene (10c)	11c	Ph	H	81
2-Methyl-1-buten-3-yne (10d)	11d	H	C(CH ₃)=H ₂	73
Diphenylbutadiyne (10e)	11e	Ph	C≡C-Ph	74
Trimethylsilylacetylene (10f)	11f	H	SiMe ₃	40
Bis(trimethylsilyl)acetylene (10g)	11g	SiMe ₃	SiMe ₃	<5

latter is the case in the reaction with **10g** where the two SiMe₃ groups apparently prohibit addition almost entirely and instead formation of phosphorus/iron clusters is observed. When only one of the bulky SiMe₃ groups is present addition of the phosphinidene does occur but results in only a modest yield (40%) of the phosphirene besides formation of mainly cluster **9**.

Interestingly, addition of **5** takes place with terminal alkynes as is evidenced by the reaction with phenylacetylene (**11c**, 81%), 2-methyl-1-buten-3-yne (**11d**, 73%), and trimethylsilylacetylene (**11f**, 40%). Such alkynes are not deprotonated by Collman's reagent.¹³ Neither does **5** insert into the rather acidic terminal C–H bond of the alkynes. We note, for example, that Ph–P=W(CO)₅ does give C–H insertion reactions with 'acidic' hydrocarbons.¹⁵ The observed additions suggest that the affinity of the in situ formed **5** for the alkyne group is rather high.

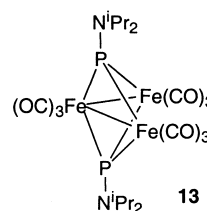
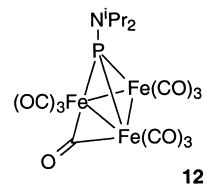
The reaction of **5** with **10d** shows that the affinity of the phosphinidene complex is higher for the alkyne group than for the olefinic group. No indications for the formation of a phosphirane were found. This reaction once again shows the similarity of ⁱPr₂N–P=Fe(CO)₄ with the established electrophilic R–P=W(CO)₅ which likewise shows a preference for the alkyne over the olefinic group.^{1a} Reaction of **3** with **4** at –30°C in the presence of a variety of olefins (such as styrene, stilbene, 2,3-dimethylbutadiene, and 1-methoxy-1,2-cyclohexadiene, except for allenes)¹⁶ does not give phosphirane products, in contrast to the addition reactions at ca. 55°C with Ph–P=W(CO)₅.¹⁷

We also explored the reaction of **5** with diphenylbutadiyne **10e**. Phosphirene formation occurs in high yield (74%) but using two or more equivalents of **5** does not lead to a second phosphinidene addition and neither is insertion in the phosphirene ring observed. Such insertions to give 1,2-dihydro-1,2-diphosphetes have been reported previously by Lammertsma¹⁸ and Mathey¹⁹ for the addition of R–P=W(CO)₅ to conjugated diynes. We conclude that **5** is less prone to give insertion reactions. The reduced reactivity of **5**, attributed to stabilization of its amine group, may further be tempered by complexation with dichlorophosphine **4**, which is present in the reaction mixture. Theoretical studies on P₂H₄ have indeed shown that the interaction between a singlet phosphinidene, ¹PH, and phosphine, PH₃, leads to a tight complex.²⁰

Changing the solvent of the reaction mixture influences the phosphirene product formation. Whereas with pentane and diethyl ether similar results are obtained this is not

the case for THF. In this solvent the reaction starts already at –85°C and gives lower yields of phosphirenes (as followed by ³¹P NMR), which is compounded by more tedious product isolations. We feel that the higher solubility of Collman's reagent in THF may enhance the Fe/P cluster formation. Monitoring the THF reaction mixture with ³¹P-NMR at –85°C shows the emergence of an intermediate product (δ=365 ppm) which disappears above –40°C, at which temperature the formation of clusters begins. We tentatively assign this low field resonance to the earlier postulated symmetrically complexed diphosphene **6** (Eq. 2).^{9a}

In almost all cases a minor, dark colored solid by-product was obtained, which was identified as the trinuclear Fe cluster **12**. Interestingly, whereas related clusters are formed from, e.g. MesPCl₂ and **3**,^{9d} they have been noted not to result from the reaction of amino dichlorophosphines R₂NPCl₂ with **3**.^{9b} Instead, mono-amino substituted Fe/P clusters like **12** are known to result from reaction of Na₂[Fe₂(CO)₈] with **3**.^{9b} However, we consistently obtained **12** and found it to be easily separated from the organic products by chromatography. In addition to this cluster we also obtained (in about equal amounts) the di-amino substituted Fe/P cluster **13**.^{9b}



This observation lends support for the formation of diphosphene **6** as an intermediate product. Similar observations were made in Power's study on diphosphenes,^{8a} which were generated from alkyl dichlorophosphines and Collman's reagent.

These diphosphene and cluster formations illustrate the subtle conditions under which **5** is generated in situ. It all depends on the availability of complexing substrates and possibly the polarity of the solvent whether **5** reacts with

suitable alkynes or dimerizes with subsequent reactions and rearrangements to Fe/P clusters.

Conclusions

The present work leads to the following general conclusions: (1) Alternative and convenient synthetic routes are available to synthesize electrophilic phosphinidene complexes in situ. The here demonstrated route makes use of Collman's reagent and dichlorophosphines. (2) In situ formation of the reactive intermediate ${}^i\text{Pr}_2\text{N}-\text{P}=\text{Fe}(\text{CO})_4$, which is not observed by ${}^{31}\text{P}$ NMR, occurs at ca. -30°C or ca. 80° lower than the CuCl-catalyzed formation of $\text{R}-\text{P}=\text{W}(\text{CO})_5$ (from its phosphanorbornadiene precursor) and ca. 140° below the corresponding uncatalyzed reaction. The limited solubility of Collman's reagent in, e.g. pentane and diethyl ether at low temperatures dictates the effectiveness of phosphinidene formation. (3) Despite its electron-releasing amino substituent, the reactivity of ${}^i\text{Pr}_2\text{N}-\text{P}=\text{Fe}(\text{CO})_4$ is electrophilic as the additions to alkynes illustrate. This behavior is analogous to the corresponding tungsten complex $\text{R}-\text{P}=\text{W}(\text{CO})_5$. The apparent lower reactivity of ${}^i\text{Pr}_2\text{N}-\text{P}=\text{Fe}(\text{CO})_4$, illustrated by its lack of reaction with simple olefins, can be attributed to (a) the lower reaction temperature, (b) the electronic stabilization provided by the amine group, and (c) the stabilization that may result from complexation with phosphines that are present in the reaction mixture. The applicability of ${}^i\text{Pr}_2\text{N}-\text{P}=\text{Fe}(\text{CO})_4$ for synthesizing thermally labile phospho-heterocycles is currently under investigation.¹⁶

Experimental

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in vacuo and liquids were distilled (under N_2) prior to use. Solvents were distilled from LiAlH_4 (pentane, diethyl ether) and sodium benzophenone (THF). NMR spectra were recorded on Bruker AC 200 (${}^1\text{H}$, ${}^{13}\text{C}$) and WM 250 spectrometers (${}^{31}\text{P}$) using SiMe_4 (${}^1\text{H}$, ${}^{13}\text{C}$) and 85% H_3PO_4 (${}^{31}\text{P}$) as external standards, IR spectra on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HRMS) on a Finnigan MAT 90 spectrometer. Elemental analyses were obtained from Microanalytisches Labor Pascher, Remagen-Bandorf (Germany).

General procedure for synthesis of phosphirenes

A suspension of $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$ dioxane (1–2 mmol) in 10–20 ml pentane or diethyl ether is treated at -78°C ($\text{CO}_2/\text{acetone}$) with dichlorodiisopropylaminophosphine (1–2 mmol) and 1–3 equivalents of the acetylene **10**. The reaction mixture is placed in a cooling bath of -30°C , slowly warmed to room temperature where it is kept for 30 min for completion, and cooled to -15°C . Work-up at this temperature includes extraction with pentane (three times), solvent evaporation, chromatography (pentane) by column (silica) or TLC (aluminum oxide 60 F) to give orange to yellow crystals (pentane) or oils of **11**.

1-Diisopropylamino-2,3-dimethylphosphirene tetracarbonyliron(0) (11a). Yield: 0.13 g (52%), orange oil. ${}^{31}\text{P}$ (CDCl_3) δ -54.4 ppm. ${}^1\text{H}$ (CDCl_3): δ 1.06 (d, ${}^3J(\text{HH})=6.79$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$) 2.24 (d, ${}^3J(\text{PH})=10.91$ Hz, 6H, $=\text{CCH}_3$) 3.51 (dsp, ${}^3J(\text{HH})=6.79$ Hz, ${}^3J(\text{PH})=16.21$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$). ${}^{13}\text{C}$ (CDCl_3): δ 15.0 (s, $=\text{CCH}_3$) 22.6 (d, ${}^3J(\text{PC})=3.2$ Hz, $\text{CH}(\text{CH}_3)_2$) 47.4 (d, ${}^2J(\text{PC})=3.9$ Hz, $\text{CH}(\text{CH}_3)_2$) 151.8 (d, ${}^1J(\text{PC})=11.8$ Hz, $=\text{CCH}_3$) 214.0 (d, ${}^2J(\text{PC})=24.7$ Hz, CO). IR (KBr) ν (CO) 2025, 2002, 1985 cm^{-1} . HRMS: calc. $\text{C}_{14}\text{H}_{20}\text{FeNO}_4$ 353.04793, found 353.04818.

1-Diisopropylamino-2,3-diphenylphosphirene tetracarbonyliron(0) (11b). Yield: 0.28 g (86%), bright yellow crystals. Mp: 101°C (decomp.). ${}^{31}\text{P}$ (C_6D_6): δ -49.4 ppm. ${}^1\text{H}$ (C_6D_6): δ 0.98 (d, ${}^3J(\text{HH})=6.85$ Hz, 12H, CH_3) 3.73 (dsp, ${}^3J(\text{HH})=6.85$ Hz, ${}^3J(\text{PH})=17.51$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$) 7.01–7.17 (m, 6H, *meta*+*para* ArH) 7.84 (d, ${}^3J(\text{HH})=6.91$ Hz, 4H, *ortho*-ArH). ${}^{13}\text{C}$ (C_6D_6): δ 23.1 (d, ${}^3J(\text{PC})=3.3$ Hz, CH_3) 48.2 (d, ${}^2J(\text{PC})=5.7$ Hz, $\text{CH}(\text{CH}_3)_2$) 129.3 (d, ${}^2J(\text{PC})=3.5$ Hz, *ipso*-C) 129.4 (s, *ortho*-Ar) 129.5 (s, *meta*-Ar) 130.6 (s, *para*-Ar) 150.7 (d, ${}^1J(\text{PC})=10.8$ Hz, C=C) 214.3 (d, ${}^2J(\text{PC})=23.5$ Hz, CO). IR (KBr) ν (CO) 2056, 1965, 1921 cm^{-1} . HRMS calc. $\text{C}_{24}\text{H}_{24}\text{FeNPO}_4$ 477.07915, found 477.07923. Elemental analysis: Cald. C, 60.40; H, 5.07; P, 6.49. Found: C, 59.74; H, 5.06; P, 6.46.

1-Diisopropylamino-2-phenylphosphirene tetracarbonyliron(0) (11c). Yield: 0.41 g (81%), bright yellow crystals. Mp: 62°C . ${}^{31}\text{P}$ (CDCl_3) δ : -48.4 . ${}^1\text{H}$ (CDCl_3): δ 1.06 (d, ${}^3J(\text{HH})=6.85$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$) 1.11 (d, ${}^3J(\text{HH})=6.80$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$) 3.73 (dsp, ${}^3J(\text{HH})=6.82$ Hz, ${}^3J(\text{PH})=17.26$ Hz, 2H, $(\text{CH}_3)_2\text{CH}$) 7.61–7.41 (m, 5H, aryl-H) 8.69 (d, ${}^2J(\text{PH})=16.63$ Hz, $=\text{CH}$). ${}^{13}\text{C}$ (CDCl_3): δ 23.1 (d, ${}^3J(\text{PC})=2.9$ Hz, CH_3) 23.4 (d, ${}^3J(\text{PC})=3.9$ Hz, CH_3) 47.9 (d, ${}^2J(\text{PC})=5.7$ Hz, $\text{CH}(\text{CH}_3)_2$) 127.3 (d, ${}^2J(\text{PC})=3.5$ Hz, *ipso*-Ar) 129.0 (s, *ortho*-Ar) 129.2 (s, *meta*-Ar) 131.0 (s, *para*-Ar) 136.5 (s, $=\text{CH}$) 163.0 (d, ${}^1J(\text{PC})=21.8$ Hz, $\text{PhC}=\text{C}$) 213.7 (d, ${}^2J(\text{PC})=23.9$ Hz, CO). IR (KBr) ν (CO) 2052, 1977, 1923 cm^{-1} . HRMS calc. $\text{C}_{18}\text{H}_{20}\text{FeNPO}_4$ 401.04793, found 401.04787. Elemental analysis: Cald. C, 53.89; H, 5.02; P, 7.72. Found: C, 53.56; H, 5.06; P, 7.76.

1-Diisopropylamino-2-(2-isopropenyl)phosphirene tetracarbonyliron(0) (11d). Yield: 0.35 g (73%), yellow oil. ${}^{31}\text{P}$ (CDCl_3) δ -47.3 . ${}^1\text{H}$ (CDCl_3): 1.02 (d, ${}^3J(\text{HH})=6.87$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$) 1.05 (d, ${}^3J(\text{HH})=6.82$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$) 1.94 (s, 3H, CH_3) 3.67 (dsp, ${}^3J(\text{HH})=6.85$ Hz, ${}^3J(\text{PH})=17.19$ Hz, 2H, $(\text{CH}_3)_2\text{CH}$) 5.55 (s, 1H, *cis* $=\text{CH}$) 5.60 (s, 1H, *trans* $=\text{CH}$) 8.42 (d, ${}^2J(\text{PH})=16.4$ Hz, 1H, PCH). ${}^{13}\text{C}$ (CDCl_3): δ 19.3 (d, ${}^3J(\text{PC})=4.5$ Hz, $=\text{CHCH}_3$) 22.7 (d, ${}^3J(\text{PC})=2.9$ Hz, $(\text{CH}_3)_2\text{CH}$) 23.2 (d, ${}^3J(\text{PC})=3.9$ Hz, $(\text{CH}_3)_2\text{CH}$) 47.8 (d, ${}^2J(\text{PC})=5.5$ Hz, $(\text{CH}_3)_2\text{CH}$) 124.3 (d, ${}^2J(\text{PC})=3.0$ Hz, PCH) 132.4 (s, $\text{CH}_3\text{C}=\text{C}$) 137.5 (s, $=\text{CH}_2$) 164.1 (d, ${}^1J(\text{PC})=21.9$ Hz, $\text{HC}=\text{CP}$) 213.7 (d, ${}^2J(\text{PC})=23.9$ Hz, CO). IR (KBr) ν (CO) 2048, 2004, 1942 cm^{-1} .

1-Diisopropylamino-2-phenylethynylphosphirene tetracarbonyliron(0) (11e). Yield: 0.32 g (74%), orange oil. ${}^{31}\text{P}$ (CDCl_3) δ -31.8 . ${}^1\text{H}$ (CDCl_3): δ 1.06 (d, ${}^3J(\text{HH})=6.82$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$) 1.19 (d, ${}^3J(\text{HH})=6.75$ Hz,

6H, (CH₃)₂CH–) 3.77 (dsp, ³J(HH)=6.79 Hz, ³J(PH)=17.43 Hz, 2H, (CH₃)₂CH–) 7.25–7.75 (m, 10H, Ar-H). ¹³C (CDCl₃): δ 22.8 (d, ³J(PC)=3.5 Hz, (CH₃)₂CH–) 23.0 (d, ³J(PC)=3.3 Hz, (CH₃)₂CH–) 48.2 (d, ²J(PC)=5.2 Hz, (CH₃)₂CH–) 73.7 (s, –CC–Ar) 81.4 (s, CC–Ar) 121.6 (s, ipso-Ar–CC) 134.2 (s, ipso-Ph) 128.3 (s, para-Ph) 129.1 (d, ⁴J(PC)=5.5 Hz, meta-Ph) 129.4 (d, ³J(PC)=11.4 Hz, ortho-Ph) 131.0 (s, meta-Ar–CC) 131.8 (s, para-Ar–CC) 132.3 (s, ortho-Ar–CC) 134.2 (s, PC–CC–Ar) 157.8 (d, ¹J(PC)=18.3 Hz, PCPh) 213.3 (d, ²J(PC)=23.0 Hz). IR (KBr) ν (CO) 2051, 1970, 1928 cm⁻¹.

1-Diisopropylamino-2-trimethylsilylphosphirene tetracarbonyliron(0) (11f). Yield 0.15 g (40%), orange oil. ³¹P (CDCl₃): δ –74.1. ¹H (CDCl₃): δ 0.23 (s, 9H, Me₃Si) 1.00 (d, ³J(HH)=6.84 Hz, 6H, CH(CH₃)₂) 1.11 (d, ³J(HH)=6.83 Hz, 6H, CH(CH₃)₂) 3.54 (dsp, ³J(HH)=6.84 Hz, ³J(PH)=16.92 Hz, 2H, CH(CH₃)₂) 9.36 (d, ²J(PH)=22.3 Hz, 1H, =CH). ¹³C (CDCl₃): δ 0.9 (s, SiCH₃) 22.9 (d, ³J(PC)=4.0 Hz, (CH₃)₂CH) 23.4 (d, ³J(PC)=2.6 Hz, (CH₃)₂CH) 47.8 (d, ²J(PC)=5.1 Hz, (CH₃)₂CH) 92.8 (s, =CH) 155.8 (d, ¹J(PC)=3.9 Hz, =CSiMe₃) 214.0 (d, ²J(PC)=24.6 Hz, CO). IR (KBr) ν (CO) 2047, 2005, 1940 cm⁻¹.

Acknowledgements

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