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Dinuclear complexes with bridging functionalized alkylidene ligands: synthesis of the phosphonium $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_3\}]SO_3CF_3$ and of the phosphinoalkylidene $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_2\}]$

Marco Bassi, Lucia Carlucci and Valerio Zanotti*
Dipartimento di Chimica Fisica ed Inorganica dell'Università, viale Risorgimento 4, 40136 Bologna (Italy)

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Abstract

Replacement of SMe_2 by phosphines PR_3 ($PR_3 = PPh_3$, $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2Ph)_3$, $PPh_2CH_2PPh_2$, $P(NEt_2)_3$) in the sulfonium $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}]SO_3CF_3$ (**1**) results in the formation of the novel phosphonium salts $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_3\}]SO_3CF_3$. The corresponding reaction of **1** with PH_3 affords a mixture of $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_3\}]SO_3CF_3$ (**3**) and the μ-phosphinoalkylidene $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_2\}]$ (**4**). Conversion of **3** to **4** is achieved by deprotonating with NEt_3 and completely reversed upon treatment with HSO_3CF_3. The phosphonium and μ-phosphinoalkylidene complexes have been characterized on the basis of their IR, ^{31}P, ^1H and ^{13}C NMR spectra.

Introduction

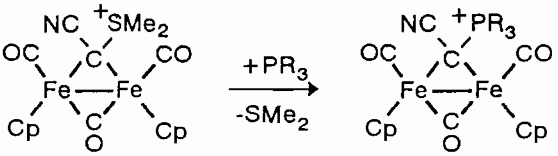
We have recently reported on the synthesis of new μ-phosphinoalkylidenes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_2\}]$ ($PR_2 = PEt_2$, PHCy, PHPh) [1] obtained by reacting the appropriate secondary or primary phosphine with the sulfonium salt $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}]SO_3CF_3$ (**1**) [2]. These reactions proceed via the deprotonation of phosphonium intermediates $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)HPR_2\}]^+$ which have been detected or isolated (in the case of the reaction with $PHEt_2$) from the reaction mixture.

Herein we report on the reactions of **1** with tertiary phosphines yielding stable phosphonium derivatives of the type $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_3\}]SO_3CF_3$. The reaction of **1** with PH_3 will also be described and discussed.

Results and discussion

Treatment of a CH_3CN solution of $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}]SO_3CF_3$ (**1**) with 1 equiv. of a tertiary phosphine led to the replacement of the SMe_2 molecule by PR_3 as shown in Scheme 1.

Compounds **2a–g** were isolated as moderately air stable red crystalline solids in 60–80% yield. Their IR spectra display a weak ν(CN) band at about 2156 cm^{-1}, and a strong-weak-medium ν(CO) band pattern (e.g. **2b**: 2003, 1974, 1833 cm^{-1}) which is common to all of the related cyanoalkylidenes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)X\}]$ (X = SR [3], OR [4], NR_2 [5], PR_2 [1]) and consistent with a *cis* configuration (Cp ligands *cis* to each other). It should be noted that the CO frequencies of the phosphonium **2a–g** are at lower wavenumbers compared to those of the parent sulfonium **1** (2013, 1981, 1835 cm^{-1} in CH_3CN) in agreement with better electron donor properties of PR_3 with respect to SMe_2. Both ^{13}C and ^1H NMR spectra of **2a–g** show one single resonance for the Cp ligands according with the presence of one single *cis*-isomer. Finally the presence of the bridging alkylidene carbon is clearly indicated by the occurrence of a doublet in the ^{13}C NMR spectra (e.g. **2c**: $\delta = 81.2$, $J(PC) = 41$ Hz) which is comparable to the value reported for the μ-carbon atom of its sulfonium precursor **1** ($\delta = 84.5$).



$PR_3 = PPh_3$ (**2a**), $PMePh_2$ (**2b**), PMe_2Ph (**2c**), PMe_3 (**2d**), $P(CH_2Ph)_3$ (**2e**), $PPh_2CH_2PPh_2$ (**2f**), $P(NEt_2)_3$ (**2g**)

Scheme 1.

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*Author to whom correspondence should be addressed.

Only a few other dinuclear μ-phosphoniumalkylidenes are known. Examples include the complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(X)PR_3\}]^+$ (X = H, Me; $PR_3 = PBu^n{}_3$, PPh_3) [6] and $[MPtCp(CO)_2(PR_3)\{\mu\text{-}C(PR_3)C_6H_4Me\text{-}4\}]^+$ ($PR_3 = PMe_3$, PMe_2Ph; M = Mn, Re) [7] which have been obtained by addition of tertiary phosphines to the μ-C carbon of the cations $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CX)]^+$ and $[MPtCp(CO)_2(PR_3)(\mu\text{-}CC_6H_4Me\text{-}4)]^+$, respectively. Thus PR_3 addition to electrophilic μ-alkylidyne carbons, or to μ-C exhibiting pseudo-alkylidyne character as in **1**, may provide a general entry into the chemistry of bridging phosphonium-alkylidene complexes. However it should be noted that the bridging carbynes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)]^+$ have been reported to react with PR_3 to form the CO substituted derivatives $[Fe_2Cp_2(PR_3)(CO)(\mu\text{-}CO)(\mu\text{-}CX)]^+$ [8].

In order to compare the reactivity of the phosphonium **2a–g** with that of the parent sulfonium **1**, the complex **2a** has been reacted with several nucleophiles including $NaBH_4$, $NBut_4CN$ and piperidine which are known to react with **1** yielding the corresponding cyanoalkylidenes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)X\}]$ (X = H, CN, $N(C_5H_{10})$) [5]. In all the cases examined treatment of **2a** with the above mentioned nucleophiles in CH_3CN at room temperature resulted in decomposition and $[FeCp(CO)_2]_2$ was the only identified product.

Compounds **2a–g** are more stable than the related phosphonium complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PHR_2]^+$ and $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_2R]^+$ [1] probably because these latter compounds easily undergo deprotonation at the phosphorus atom. In order to better understanding the influence of phosphines containing P–H bonds upon the stability of the phosphonium complexes we decided to investigate the reaction of **1** with PH_3. When phosphorous trihydride (PH_3) was slowly bubbled through a solution of **1** in CH_3CN for about 2 h the color of the mixture turned bright red. The IR spectrum of the reaction mixture exhibited two sets of absorption at 2166w, 2005s, 1828m and 2143w, 1989s, 1957w, 1798m cm^{-1} attributable to the phosphonium $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_3]^+$ (**3**) and to the phosphinocarbene $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_2]$ (**4**), respectively. As analogously observed in the case of $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_2Ph\}]^+$ [1], the phosphonium $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PH_3\}]^+$ (**3**) underwent partial deprotonation, under the reaction conditions. However, even in the presence of a large excess of PH_3 the deprotonation was not complete. In order to obtain an almost quantitative conversion of **3** to **4**, NEt_3 was added to the reaction mixture. Filtration through an alumina pad and crystallization from CH_2Cl_2/n-pentane gave **4** in 41% yield. Deprotonation of the P atom was reversed upon treatment with HSO_3CF_3. Compound **3** was conveniently prepared by treatment of **4** with HSO_3CF_3, however any attempts to obtain pure crystalline samples of **3** failed. The IR spectrum of **4**, in CH_2Cl_2, shows ν(CO) bands at 1993, 1963, 1799 and a ν(CN) absorption at 2143 cm^{-1}. In the ^1H NMR spectrum of **4** a doublet for the PH_2 protons is observed at $\delta = 5.23$ with $J(PH) = 212$ Hz which is strictly comparable with the P–H coupling constants reported for the related phosphinoalkylidene complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PHCy\}]$ ($J(PH) = 198$ Hz) and $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PHPh\}]$ ($J(PH) = 204$ Hz) [1]. The ^{13}C NMR spectrum of **4** exhibits a doublet for the μ-alkylidene carbon at $\delta = 120.4$ ($J(PC) = 64$ Hz) which is in agreement with the values reported for the corresponding μ-carbon atoms in related phosphinoalkylidene complexes (e.g. δ 120.1, $J(PC) = 62$ Hz for $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PEt_2\}]$ [1]). Moreover two signals of different intensities (approximately 9:1 ratio) are observed in the Cp region (at 92.0 and 91.9, respectively) although only a single peak for Cp appears in the ^1H NMR spectrum ($\delta = 4.95$) suggesting the presence of a mixture of isomers. These are likely the two *cis*-isomers since the *trans*-isomer is expected to give rise to two equally intense Cp resonances. The ^{31}P NMR of **4** ($CDCl_3$) also indicates the presence of two isomers since two resonances of different intensities are shown at $\delta = 64.0$ (main isomer) and 61.4. The *cis*-isomer bearing the CN group on the Cp side is presumably the most abundant since, for this class of compounds, it has been observed that isomeric distribution is determined by steric hindrance of the substituents of the μ-alkylidene carbon [5, 9].

Experimental

All reactions were routinely carried out under nitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. IR spectra were recorded on a Perkin-Elmer 983-G. NMR spectra were recorded on a Varian Gemini 200 spectrometer. Elemental analyses were determined by the Pascher Microanalytical Laboratorium (Remagen, Germany). The compound $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}]SO_3CF_3$ (**1**) was prepared by a published method [2].

Synthesis of $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PPh_3\}]SO_3CF_3$ *(2a)*

To a solution of **1** (0.23 g, 0.40 mmol) in CH_3CN (15 ml) was added PPh_3 (0.13 g, 0.51 mmol). The mixture was stirred for 5 min and evaporated to dryness under vacuum. The red oily residue was washed with n-pentane (3×5 ml) and crystallized from CH_2Cl_2/n-pentane mixture at −20 °C yielding red crystals of **2a** (0.21 mg, 69%). *Anal.* Found: C, 53.0; H, 3.4. Calc. for $C_{34}H_{25}F_3Fe_2NO_6PS$: C, 52.67; H, 3.25%. IR (cm^{-1}, CH_2Cl_2): ν=2152w (CN); 2012s, 1982w, 1828m (CO). ^{1}H NMR (CD_3COCD_3): δ=8.21–7.83 (m, 15H, Ph), 5.68 (s, 10H, Cp). ^{13}C NMR (CD_3COCD_3): δ=255.8 (μ-CO), 209.7 (d, *J*(PC)=5.5 Hz, CO), [136.5 (d, *J*(PC)=8.8 Hz), 135.7 (d, *J*(PC)=2.0 Hz), 130.8 (d, *J*(PC)=11.9 Hz), 124.7 (d, *J*(PC)=83.7 Hz) Ph], 94.9 (Cp).

Synthesis of [$Fe_2Cp_2(CO)_2(\mu$-$CO)\{\mu$-$C(CN)X\}]SO_3CF_3$ (X=$PMePh_2$ (2b), PMe_2Ph (2c), PMe_3 (2d), $P(CH_2Ph)_3$ (2e), $PPh_2CH_2PPh_2$ (2f), $P(NEt_2)_3$ (2g)

These complexes were obtained by the procedure described for the synthesis of **2a**.

2b. Yield 70%. *Anal.* Found: C, 48.6; H, 3.3. Calc. for $C_{29}H_{23}F_3Fe_2NO_6PS$: C, 48.83; H, 3.25%. IR (cm^{-1}, CH_2Cl_2): ν=2157w (CN); 2003s, 1974w, 1833m (CO). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ=8.00–7.60 (m, 10H, Ph), 4.93 (s, 10H, Cp), 1.90 (d, *J*(PH)=13 Hz, 3H, Me). ^{13}C NMR (CD_2Cl_2): δ=211.1 (CO), [135.7, 132.9 (d, *J*(PC)=8 Hz), 131.2 (d, *J*(PC)=11 Hz), 136.9 (d, *J*(PC)=40 Hz) Ph], 94.0 (Cp), 13.1 (d, *J*(PC)=62 Hz, Me). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ=46.8.

2c. Yield 81%. *Anal.* Found: C, 44.2; H, 3.7. Calc. for $C_{24}H_{21}F_3Fe_2NO_6PS$: C, 44.27; H, 3.25%. IR (cm^{-1}, CH_3CN): ν=2157w (CN); 2001s, 1968w, 1828m (CO). ^{1}H NMR (CD_3CN): δ=8.11–7.80 (m, 5H, Ph), 5.13 (s, 10H, Cp), 2.28 (d, *J*(PH)=12 Hz, 6H, Me). ^{13}C NMR (CD_3CN): δ=254.6 (μ-CO), 210.0 (d, *J*(PC)=6 Hz, CO), [134.1 (d, *J*(PC)=2.5 Hz), 130.8 (d, *J*(PC)=8.5 Hz), 129.5 (*J*(PC)=11.5 Hz), 126.3 (*J*(PC)=81 Hz) Ph], 92.6 (Cp), 81.4 (d, *J*(PC)=41 Hz, μ-C), 10.9 (d, *J*(PC)=58 Hz, Me).

2d. Yield 56%. *Anal.* Found: C, 37.9; H, 3.4. Calc. for $C_{19}H_{19}F_3Fe_2NO_6PS$: C, 38.74; H, 3.25%. IR (cm^{-1}, CH_3CN): ν=2156w (CN); 2001s, 1969w, 1828m (CO). ^{1}H NMR (CD_3CN): ν=5.34 (s, 10H, Cp), 2.08 (d, *J*(PH)=12.6 Hz, 9H, Me). ^{13}C NMR (CD_3CN): δ=255.1 (μ-CO), 210.1 (d, *J*(PC)=6 Hz, CO), 130.0 (CN), 92.7 (Cp), 79.2 (d, *J*(PC)=44 Hz, μ-C), 12.7 (d, *J*(PC)=57 Hz, Me).

2e. Compound **2e** was crystallized from CH_3CN layered with Et_2O. Yield 74%. *Anal.* Found: C, 53.9; H, 3.8. Calc. for $C_{37}H_{31}F_3Fe_2NO_6PS$: C, 54.37; H, 3.82%. IR (cm^{-1}, CH_2Cl_2): ν=2152w (CN); 1998s, 1969w, 1834m (CO). ^{1}H NMR (CD_3CN): δ=7.50–7.15 (m, 15H, Ph), 5.15 (s, 10H, Cp), 3.61 (d, *J*(PH)=13 Hz, 6H, *C*H_2Ph). ^{13}C NMR (CD_3CN): δ=253.5 (μ-CO), 211.3 (CO), 131.0, 129.9, 129.0 (Ph), 124.5 (CN), 93.2 (Cp), 75.2 (d, *J*(PC)=22 Hz, μ-C), 32.0 (d, *J*(PC)=44 Hz, *C*H_2Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ=49.9.

2f. Compound **2f** was crystallized from CH_3CN layered with Et_2O. Yield 81%. *Anal.* Found: C, 54.5; H, 4.0. Calc. for $C_{41}H_{32}F_3Fe_2NO_6P_2S$: C, 54.87; H, 3.59%. IR (cm^{-1}, CH_3CN): ν=2155w (CN); 1996s, 1963w, 1829m (CO). ^{1}H NMR (CD_2Cl_2): δ=8.06–6.89 (m, 20H, Ph), 4.98 (s, 10H, Cp), 2.90 (d, *J*(PH)=12.8 Hz, 2H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ=51.0 (d, *J*(PP)=69 Hz), −24.4 (d, *J*(PP)=69 Hz).

2g. Yield 55%. *Anal.* Found: C, 44.6; H, 5.1. Calc. for $C_{28}H_{40}F_3Fe_2N_4O_6PS$: C, 44.23; H, 5.30%. IR (cm^{-1}, CH_2Cl_2): ν=2147w (CN); 2002s, 1977w, 1827m (CO). ^{1}H NMR ($CDCl_3$): δ=5.31 (s, 10H, Cp), 3.3 (m, br, 12H, CH_2CH$_3$), 1.3 (m, br, 18H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$): δ=253.8 (μ-CO), 211.8 (d, *J*(PC)=6 Hz, CO), 132.9 (CN), 94.5 (Cp), 85.7 (d, *J*(PC)=88 Hz, μ-C), 41.7 (*C*H$_2$CH$_3$), 13.3 (CH$_2$*C*H$_3$).

Synthesis of [$Fe_2Cp_2(CO)_2(\mu$-$CO)\{\mu$-$C(CN)PH_2\}$] (4)

Through a stirred solution of **1** (0.37 g, 0.64 mmol) in CH_3CN (50 ml) under a stream of dinitrogen, PH_3 was slowly bubbled for about 100 min. **Caution**: PH_3 is extremely toxic and spontaneously ignites in air. The mixture was stirred for an additional 60 min and treated with an excess of NEt_3 (0.15 g, 1.48 mmol). The volatile material was then removed *in vacuo*. The residue was redissolved in CH_2Cl_2 and the solution filtered through an alumina pad (3×5 cm). The filtered red solution was reduced to minimum volume, layered with n-pentane and cooled to −20 °C affording red crystals of complex **4** (0.10 g, 41%). *Anal.* Found: C, 45.3; H, 3.2. Calc. for $C_{15}H_{12}Fe_2NO_3P$: C, 45.39; H, 3.05%. IR (cm^{-1}, CH_2Cl_2): ν=2143w (CN); 1993s, 1963w, 1799m (CO). ^{1}H NMR (CD_3CN): δ=5.29 (d, *J*(PH)=212 Hz, 2H, PH), 5.07 (s, 10H, Cp). ^{13}C NMR (CD_2Cl_2): δ=266.5 (μ-CO), 211.3 (CO), 210.4 (d, *J*(PC)=16 Hz, CO) 135.4 (br, CN), 120.0 (d, *J*(PC)=64 Hz, μ-C), 92.0 (Cp). Signals of lower intensity (9:1) at 211.2 (CO) and 91.9 (Cp) due to the *cis*-isomer bearing the PH_2 group on the Cp side are also observed). ^{31}P{^{1}H} NMR ($CDCl_3$): δ=64.0 (major isomer), 61.4 (minor isomer).

Synthesis of [$Fe_2Cp_2(CO)_2(\mu$-$CO)\{\mu$-$C(CN)PH_3\}]SO_3CF_3$ (3)

Complex **3** was better prepared by treating a CH_2Cl_2 solution (20 ml) of **4** (0.18 g, 0.45 mmol) with HSO_3CF_3 (0.07 g, 0.50 mmol). The mixture was stirred for 10 min and evaporated to dryness *in vacuo* and the residue washed with n-pentane. Attempts to crystallize the oily, red residue from CH_2Cl_2/n-pentane failed. Yield 0.23 g, 93%. IR (cm^{-1}, CH_3CN): ν=2166w (CN); 2005s, 1989sh, 1828m (CO). ^{1}H NMR (CD_3CN): δ=6.40 (d, *J*(PH)=494 Hz, 3H, PH), 5.33 (s, 10H, Cp).

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