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REACTIONS OF BIS(DIPHENYLPHOSPHINE)ACETYLENE WITH METAL CARBONYL COMPLEXES

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The reaction of $[\text{Co}_2(\text{CO})_8]$ with DPPA at room temperature yields a diphosphine bridged product $[\text{Co}_4(\text{CO})_{12}(\mu\text{-Ph}_2\text{-P-C}\equiv\text{C-P-Ph}_2)_2]$ **1**. Heating of **1** at 45°C promoted cleavage of the P–C_{sp} bond with the formation of binuclear, phosphido-bridged σ - π -acetylide isomer complexes $[\text{Co}_2(\text{CO})_5(\mu\text{-PPh}_2)(\mu\text{-}\sigma\text{-}\pi\text{-C}\equiv\text{C-PPh}_2)]$ **2a**, **2b**. Heating (60°C) of the complex $[\text{CpFe}(\text{CO})_2\text{CH}_3]$ and DPPA affords mono and binuclear acetyl, *P*-coordinated diphenylphosphinoalkyne metal complexes $[\text{CpFe}(\text{Ph}_2\text{P-C}\equiv\text{C-PPh}_2)\text{CO}(\text{COCH}_3)]$ **3**, $[\text{CpFeCO}(\text{COCH}_3)]_2\text{-}\mu\text{-(Ph}_2\text{P-C}\equiv\text{C-PPh}_2)$ **4**.

Keywords: Bis(diphenylphosphine)acetylene; Metal carbonyl complexes; Iron; Cobalt

INTRODUCTION

Our interest in alkyne chemistry [1–7] prompted us to investigate the behavior of bis(diphenylphosphine)acetylene, (DPPA), towards some metal-carbonyl complexes. DPPA is a potentially tridentate ligand, whose coordination capability has been extensively studied [8–11]. The typical behavior of this nonchelating disubstituted acetylene is to form bridged binuclear or polymeric complexes in which only the two phosphorus atoms of the ligand are coordinated with the acetylenic bond coordinatively inactive. It is conceivable, however, that DPPA might coordinate via its triple bond if the phosphorus lone pairs were first blocked by strongly coordinated sixteen-electron fragments. Such compounds might then react via their alkyne function to form clusters. To test this possibility, we prepared some carbonyl complexes of DPPA, whose syntheses and structures are reported.

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EXPERIMENTAL

General Procedures

All reactions were carried out under an atmosphere of dry N₂ by using standard Schlenk techniques. Solvents were dried and distilled under N₂ from appropriate drying agents. Chromatographic separations and purification were effected using Florisil, under an atmosphere of dry N₂. Microanalyses were performed on a Perkin Elmer 2400 CHN. Metal determinations were obtained by Atomic Absorption Spectroscopy using a Varian AAG and a Hitachi Z8200. IR spectra were recorded on a FTIR 3000 Mattson Instrument (from 400 to 4000 cm⁻¹) and on a Perkin Elmer 283B (from 200 to 4000 cm⁻¹). NMR spectra were recorded on a Varian EM-360 A (60 MHz) and on a AC-80FT-NMR Spectrophotometer (80 MHz) and Bruker DRX400 using the pulsed FTNMR technique for ¹H, ¹³C and ³¹P. Chemical shift data are quoted in δ units, with positive values to low field of the indicated reference (solvent and TMS, 85% H₃PO₄ solution, respectively) and were corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hertz. Mass spectra were recorded with a Hewlett Packard-5889-A mass spectrometer and taken at 70 eV by insertion techniques. Raman spectra were recorded on a Raman Renishaw instrument equipped with a microscope and a CCP type detector, in the 200–2500 cm⁻¹ range. All materials used in this work were either commercial samples or prepared by well-established procedures.

Reaction of [Co₂(CO)₈] with DPPA

Gas was evolved upon treating a THF (200 mL) solution of [Co₂(CO)₈] (0.60 g; 1.75 mmol) with DPPA (0.70 g; 1.78 mmol) under mild conditions (room temperature, reduced pressure). After gas evolution ceased, the solution was stirred for 2.75 h more. After complete evaporation of the solvent, the residue was washed with hexane yielding a bright brown solid of complex [Co₄(CO)₁₂(μ-Ph₂-P-C≡C-P-Ph₂)₂] **1** (yield: 86%, decomposition: ~230°C). Anal. Calcd. for C₆₄H₄₀O₁₂P₄Co₄ **1** (1360) (%): C, 56.48; H, 2.94; Co, 17.33; found: C, 55.16; H, 3.11; Co, 17.48.

Thermal Transformation of **1**

Heating (45°C/3 h) of Complex **1** (0.43 g; 0.32 mmol) in 250 mL of THF leads to the formation of a mixture containing two isomers **2a** and **2b**. Upon complete evaporation of the solvent, the mixture was washed with hexane to afford a brown crystalline solid. Unfortunately, **2a** and **2b** could not be separated by chromatography (CH₂Cl₂) or recrystallization (CH₂Cl₂-hexane) – (yield: 84%) (decomposition: 275–280°C). Anal. Calcd. for C₃₂H₂₀O₆P₂Co₂ **2** (680) (%): C, 56.50; H, 2.94; Co, 17.33; found: C, 54.81; H, 3.57; Co, 17.83.

Reaction between [CpFe(CO)₂CH₃] and DPPA

A solution of [CpFe(CO)₂CH₃] (0.28 g, 1.46 mmol) and DPPA (0.57 g, 1.45 mmol), in 250 mL CH₂Cl₂, was heated (60°C) for 5h. The solvent was then removed under

vacuum and the residue washed with hexane to extract **3** [$\text{CpFe}(\text{PPh}_2\text{C}\equiv\text{CPh}_2)\text{CO}(\text{COCH}_3)$] which was subsequently isolated as an orange solid after removal of hexane (yield = 4%) (decomposition: 116–121°C). Column chromatography, eluted with $\text{CH}_2\text{Cl}_2\text{--THF}$ (20:1), of the residue gave the dinuclear Complex **4** [$\text{CpFeCO}(\text{COCH}_3)_2\text{--}\mu\text{--}(\text{Ph}_2\text{P--C}\equiv\text{C--PPh}_2)$] as a yellow-orange crystalline solid (yield = 80%) (decomposition: 157°C).

Alternatively, **3** and **4** could be obtained when the reaction was carried out without solvent at 88°C, with different yields depending on the reaction times (1.5 h: **3** = 90%, **4** = 4%; 2.5 h: **3** = 4%, **4** = 85%). Anal. Calcd. for $\text{C}_{32}\text{H}_{28}\text{O}_2\text{P}_2\text{Fe}$ **3** (562) (%): C, 68.35; H, 4.98; Fe, 9.93; found: C, 68.19; H, 4.41; Fe, 9.80 and $\text{C}_{42}\text{H}_{36}\text{O}_4\text{P}_2\text{Fe}_2$ **4** (778) (%): C, 64.78; H, 4.62; Fe, 14.39; found: C, 64.82; H, 4.35; Fe, 14.22. Mass spectra: *Complex 3*: (*m/e*): $[\text{CC--P}]^+$: 55; 73; $[\text{FeCO}]^+$: 83; $[\text{Fe--P--CC}]^+$: 111; $[(\eta^5\text{-C}_5\text{H}_5)\text{FeP}]^+$: 152; $[\text{PPh}_2]^+$: 185; $[\text{CC--PPh}_2]^+$: 209; $[(\eta^5\text{-C}_5\text{H}_5)\text{FeCOPCCP}]^+$: 236; $[(\eta^5\text{-C}_5\text{H}_5)\text{FeCOPPh}]^+$: 256; $[\text{Ph}_2\text{PCCPPh}_2]^+$: 394. *Complex 4*: (*m/e*): $[\text{CCP}]^+$: 55; $[\text{FeCO}]^+$: 83; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}]^+$: 121; $[\text{Fe--P--C}_6\text{H}_5]^+$: 164; $[\text{CC--PPh}_2]^+$: 209; 256; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{COCH}_3)\text{P}]^+$: 284; 368; $[\text{Ph}_2\text{PCCPPh}_2]^+$: 394; $[\text{Fe--PPh}_2\text{CCPPh}_2]^+$: 450.

RESULTS AND DISCUSSION

Reaction of $[\text{Co}_2(\text{CO})_8]$ with DPPA

This reaction yielded a bisdiphosphine-bridged product $[\text{Co}_4(\text{CO})_{12}(\mu\text{-Ph}_2\text{P--C}\equiv\text{C--PPh}_2)_2]$ **1**. IR spectra of Complex **1** in the CO stretching region show absorptions characteristic of terminal and bridging CO groups (Table I). NMR spectroscopic data are summarized in Table II. Due to rapid decomposition of **1**, in CDCl_3 , a detailed analysis of its ^{13}C NMR spectrum was not possible. Microanalyses and spectroscopic data support the proposed structure in which two diphosphines bridge two $\text{Co}_2(\text{CO})_6$ units symmetrically. Furthermore, the well established ligand geometry and nonchelating properties of the ligand favors the structure shown in Scheme 1.

TABLE I Infrared and Raman Spectroscopic data for Compounds **1**, **2a**, **2b**, **3**, **4a**, **4b** (cm^{-1})

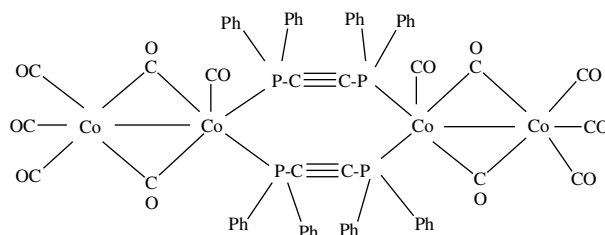
Compound	$\nu\text{C}\equiv\text{C}$		$\nu\text{CO}(\text{terminal})$		$\nu\text{CO}(\text{bridged})$		$\nu\text{CO}(\text{acetyl})$		$\nu\text{C}=\text{C}$	
	a	b	a	b	a	b	a	b	a	b
1			1970(S)	1990(S)						
			1980(S)	2020(S)	1790(S)	1775(W)				
			2000(S)	2050(S)	1820(S)	1795(S)				
			2020(S)	2080(S)		1815(S)				
			2085(S)			1845(S)				
2a, 2b			1960(Sh)	1980(Sh)						
			1980(S)	2013(S)					1535(Sh)	
			2000(S)	2026(S)						
			2040(mS)	2060(m)						
3	2090(W)	2090(W)	1920(S)	1930(S)			1600(S)	1600(mS)		
4a, 4b	2117 ^c		1913 ^c				1585 ^c	1600(m)		
			1925(S)	1935(S)			1600(m)			

^aKBr; ^b $\text{CH}_2\text{Cl}_2\text{--CsI}$; ^cRaman Spectroscopy.

TABLE II ^1H , ^{13}C {H} and ^{31}P {H} NMR data (δ in ppm and J in Hz) for Complexes **1**, **2a**, **2b**, **3**, **4a**, **4b** (CDCl_3)

Compound	^1H NMR	^{13}C {H} NMR	^{31}P {H} NMR
1	7.2–7.7 (m, Ph) ^c	123.0–137.5 (m, Ph) ^c , 210.65 (s, CO)	53.56 (s) ^b
2a	7.0–7.8 (m, Ph) ^c	123.0–137.0 (m, Ph) ^b	–33.02 (d, 1P), $J_{\text{PP}} = 51.90$ Hz, 42.91 (d, 1P) ^b , $J_{\text{PP}} = 51.90$ Hz
2b	7.0–7.8 (m, Ph) ^c	123.0–137.0 (m, Ph) ^b	23.00 (s, 1P), 134.60 (s, 1P)
3	2.15 (s, Me) ^c , 4.48 (d, Cp), $J_{\text{HP}} = 1.38$ Hz, 7.2–8.0 (m, Ph)	51.32 (d, Me) ^c , $J_{\text{CP}} = 4.93$ Hz, 85.42 (s, Cp); 103.81 (C1, dd), $J_{\text{C1P1}} = 67.61$ Hz, $J_{\text{C1P2}} = 0.30$ Hz, 108.74 (C2, dd), $J_{\text{C2P2}} = 21.13$ Hz, $J_{\text{C2P1}} = 6.04$ Hz, 125.0–138.0 (m, Ph), 219.00 (d, FeCO), $J_{\text{CP}} = 30.18$ Hz, 273.65 (d, Fe–COMe), $J_{\text{CP}} = 25.15$ Hz	–32.61 (s) ^c , 60.09 (s)
4a, 4b	2.15 (s, Me), 2.16 (s, Me) ^c , 4.55 (d, Cp), $J_{\text{HP}} = 1.32$ Hz, 4.57 (d, Cp), $J_{\text{HP}} = 1.42$ Hz, 7.0–7.9 (m, Ph)	51.75 (d, Me), $J_{\text{CP}} = 5.27$ Hz, 51.76 (d, Me) ^c , $J_{\text{CP}} = 5.27$ Hz, 85.61 (s, Cp), 85.64 (s, Cp), 125.7–137.7 (m, Ph), 219.10 (d, Fe–CO), $J_{\text{CP}} = 30.28$ Hz, 219.14 (d, Fe–CO), $J_{\text{CP}} = 30.28$ Hz	59.62 (s) ^c , 60.32 (s)

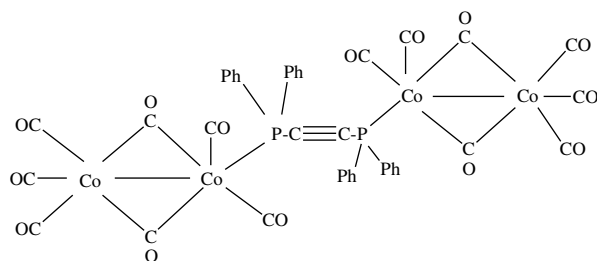
^a60 MHz; ^b80 MHz; ^c400 MHz, δ_{H} and $\delta_{^{13}\text{C}}$: ppm/TMS; $\delta_{^{31}\text{P}}$: ppm/ H_3PO_4 .



1

SCHEME 1

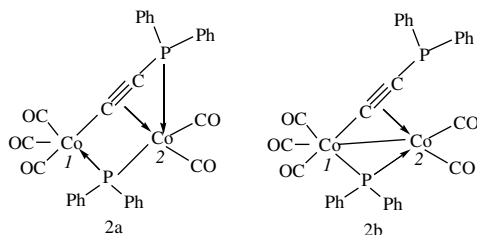
Carty and co-workers [12] reported the first example of monosubstituted complex containing bridging DPPA, i.e. $[\text{Co}_2(\text{CO})_7](\mu\text{-DPPA})$, which is closely related to **1**. However, the latter contains two bridging DPPA bonded through phosphorus (*viz*) (Scheme 1a).



SCHEME 1a

Thermal Study of $[\text{Co}_4(\text{CO})_{12}(\mu\text{-Ph}_2\text{-P-C}\equiv\text{C-P-Ph}_2)_2]$ **1**

Heating of **1** affords $[\text{Co}_2(\text{CO})_5(\mu\text{-PPh}_2)(\mu\text{-}\sigma\text{-}\pi\text{-C}\equiv\text{C-PPh}_2)]$ **2a**, **2b** as a mixture of two isomers. The binuclear Complexes **2a**, **2b** contain a phosphido-bridge and a $\sigma\text{-}\pi$ -acetylide ligand that result from cleavage of the P-C_{sp} bond [9,10]. A new band in the IR spectrum found at 1535 cm^{-1} (Table I) attributed to $\nu(\text{C}=\text{C})$ and the absence of a band higher than 2100 cm^{-1} , characteristic of $\nu(\text{C}\equiv\text{C})$, suggest the coordination of the triple bond of the acetylide to $\text{Co}(2)$ in **2a** and **2b** (viz). $^{31}\text{P}\{\text{H}\}$ NMR spectrum shows two sets of two signals, each one may be attributed to one of the isomers present in solution in the proportion 2:1 **2a:2b** (Table II) (Scheme 2).



SCHEME 2

The chemical shift found for $\mu\text{-PPh}_2$ in **2b** (δ 134.60) is characteristic of a PPh_2 ligand bridging two metals joined by a metal-metal bond. On the other hand, **2a** shows a chemical shift at δ -33.02 consistent with a $\mu\text{-PPh}_2$ bridging two metals not joined by a metal-metal bond. Numerous correlations have shown that the $\mu\text{-PPh}_2$ ligands in compounds with metal-metal bonds show chemical shifts between δ 50 and δ 300, whereas those without a metal-metal bond have chemical shifts between δ 50 and δ -200 [13,14].

The proposal of a $\text{Co}(2)\text{-P}(\text{acetylide})$ bond in **2a** is based on the chemical shift found for the $\text{P}(\text{acetylide})$ (δ 42.91) and on its $^2J_{\text{PP}}$ coupling constant. The proposed structure for **2a** implies an intramolecular interaction $\text{P-Co}(2)$ generating a highly strained C-Co-P ring. Although the spectroscopic studies of **2a** unequivocally point to coordination through both the $\text{C}\equiv\text{C}$ and phosphorus in the complex, a structure involving an intermolecular phosphorus coordination (Fig. 1) cannot be ruled out.

The less positive value for the $\delta_{\text{P}(\text{acetylide})}$ (δ 23.00) found for **2b**, in comparison to **2a**, and the absence of a $^2J_{\text{PP}}$ coupling constant suggest that the $\text{P}(\text{acetylide})$ is not bonded through $\text{Co}(2)$. The positive chemical shift $\delta_{\text{P}(\text{acetylide})}$ observed for **2b** can be

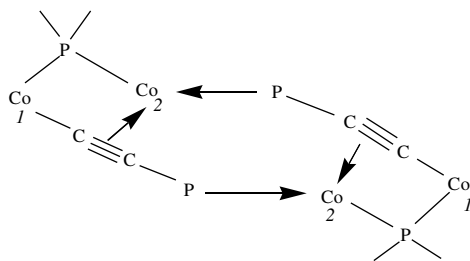


FIGURE 1 Possible intermolecular interaction for Complex **2a**.

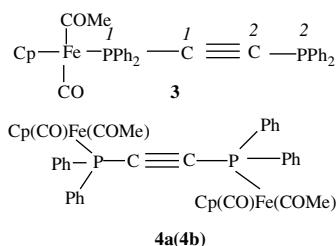
understood as resulting from the interaction between $C\equiv C$ and the cobalt atom. In fact, the shielding of the ^{31}P nucleus is sensitive to electronic density variations in the neighboring $C\equiv C$ bond [15,16].

Unfortunately a good ^{13}C NMR spectrum for **2** could not be obtained (Table II).

Reaction of $[\text{CpFe}(\text{CO})_2\text{CH}_3]$ with DPPA

Heating of $[\text{CpFe}(\text{CO})_2\text{CH}_3]$ with DPPA, in CH_2Cl_2 , at 60°C for 5h, affords $[\text{CpFe}(\text{Ph}_2\text{P}-\text{C}\equiv\text{C}-\text{PPh}_2)\text{CO}(\text{COCH}_3)]$ **3** and $[\text{CpFeCO}(\text{COCH}_3)]_2-\mu-(\text{Ph}_2\text{P}-\text{C}\equiv\text{C}-\text{PPh}_2)$ **4**, the latter as a mixture of diastereomers (RR/RS and RS/SR pairs) **4a**, **4b** (Scheme 3). Alternatively, the reaction can be carried out without solvent, yielding **3** and **4** in different proportions, depending on the reaction times (*vide infra*), suggesting that **3** undergoes a subsequent reaction to give the dinuclear acetyl product **4**.

Infrared spectra of **3** show a band due to the terminal carbonyl and a band due to an acetyl group. The expected lowering of $\nu\text{CO}(\text{terminal})$ (Table I) is consistent with the coordination of a phosphine to the metallic center. The presence of a band at 2090 cm^{-1} , characteristic of $\nu\text{C}\equiv\text{C}$ denotes the noncoordination of DPPA through the unsaturated system $C\equiv C$ but via only one phosphorus atom from DPPA, which is also confirmed by the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of **3**, that consists of two singlets ($\delta_{\text{P}1}$ 60.09 and $\delta_{\text{P}2}$ -32.61) (*vide* Table II).



SCHEME 3

The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **3** also shows that one of the P nuclei is not bonded through the iron, since two doublets of doublets are observed for C1 and C2 at δ 103.81 and δ 108.74, respectively as found for similar complexes [11,17].

The ^1H NMR data (Table II) support the proposed structure for **3** and show an increasing of the δ_{Me} in relation to $[\text{CpFe}(\text{CO})_2\text{CH}_3]$ (δ_{Me} 0.16; δ_{Cp} 4.60), as expected for acetyl complexes. The coordination of the DPPA, via P-lone-pair, results on a smaller δ_{Cp} , as expected.

The absence of the $\nu\text{C}\equiv\text{C}$ on the IR spectrum of **4a**, **4b** and the presence of a band at 2117 cm^{-1} on its Raman spectrum suggest that DPPA takes a symmetrical position between the metallic centers of iron.

The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of **4** shows two singlets (in the ratio of 1:1), suggesting a mixture of two isomers and each singlet corresponds to the equivalent phosphorus nuclei of each isomer. Similar conclusions can be drawn from the ^1H and $^{13}\text{C}\{\text{H}\}$ NMR data for **4**. Unlike **4**, $[\text{CpMo}(\text{CO})_2(\text{COCH}_3)]_2-\mu\text{-DPPA}$ is not formed as a mixture of diastereomers [18].

One might expect that $[\text{CpFeCO}(\text{CH}_3)_2\mu\text{-}(\text{PPh}_2\text{C}\equiv\text{CPh}_2)]$ would be formed from decarbonylation of **4** on heating. However, **4** was partially converted to **3** by refluxing in toluene or by UV irradiation. Similarly, $[\text{CpFeCO}(\text{PPh}_3)(\text{COCH}_3)]$ does not undergo decarbonylation [19]. Rearrangements involving the cleavage of the phosphorus–alkyne bond, as observed for **1**, could also be expected [9,10], but they have not been observed.

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