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PMe_3-induced CO insertion and CO deinsertion in the zwitterionic hydrocarbyl complex $Co_2(CO)_4$ [μ-PhC=C(H)PPh_2CC(PPh_2)C(O)OC(O)]: Syntheses and X-ray structures of $Co_2(CO)_3(PMe_3)$[μ-PhC(CO)=C(H)PPh_2C=C(PPh_2)C(O)OC(O)] and $Co_2(CO)_3(PMe_3)$[μ-PhC=C(H)PPh_2C=C(PPh_2)C(O)OC(O)]

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Abstract

Treatment of the zwitterionic hydrocarbyl compound $Co_2(CO)_4$[μ-PhC=C(H)PPh_2C=C(PPh_2)C(O)OC(O)] (**1**) with PMe_3 leads to CO insertion and formation of the acyl species $Co_2(CO)_3(PMe_3)$[μ-PhC(CO)=C(H)PPh_2C=C(PPh_2)C(O)OC(O)] (**2**). Compound **2** is unstable at elevated temperatures and loses CO to produce the PMe_3-substituted compound $Co_2(CO)_3(PMe_3)$[μ-PhC=C(H)PPh_2C=C(PPh_2)C(O)OC(O)] (**3**) as the major product. Compounds **2** and **3** have been isolated and characterized in solution by IR and NMR (^{13}C and ^{31}P) spectroscopies and in the solid state by X-ray diffraction analyses.

Keywords: Diphosphine ligand; CO insertion; Ligand substitution; Cobalt complexes

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1. Introduction

Transition-metal compounds containing a hydrocarbyl moiety remain under active investigation due to their importance as intermediates in Fischer–Tropsch chemistry, coupled with the fact that they serve as synthetically useful platforms for the construction of diverse organic compounds [1]. Several years ago, we published our findings on the intramolecular attack of the diphosphine ligand bma [2,3-bis(diphenylphosphino)maleic anhydride] on coordinated alkynes in the dicobalt compounds $Co_2(CO)_4$(bma)(μ-RCCH) (where R = Ph, Bu^t) [2,3]. The nucleophilic addition of one of the phosphine moieties to the terminal alkyne carbon occurs regioselectively to furnish the zwitterionic hydrocarbyl compounds $Co_2(CO)_4$[μ-RC=C(H)PPh_2C=C(PPh_2)C(O)OC(O)]. That the nature of the alkyne ligand is critical in directing the course of these reactions was demonstrated by thermolysis of the related compound $Co_2(CO)_4$(bma)(μ-PhCCPh), where P–C bond cleavage instead of alkyne attack gives $Co_2(CO)_4$[μ-(*Z*)-Ph_2PC(Ph)=C(Ph)C=C(PPh_2)C(O)OC(O)] [4]. Here, the formal insertion of the diphenylacetylene ligand into the Ph_2P–C(maleic anhydride) bond gives rise to the eight-electron 2-[(*Z*)-1,2-diphenyl-2-(diphenylphosphino)ethenyl]-3-(diphenylphosphino)maleic

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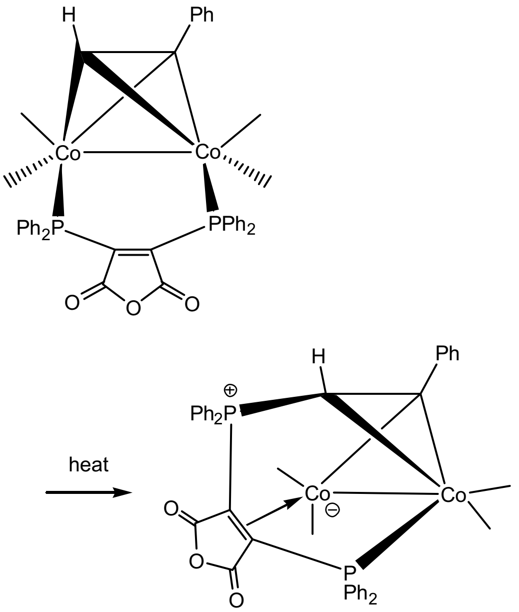
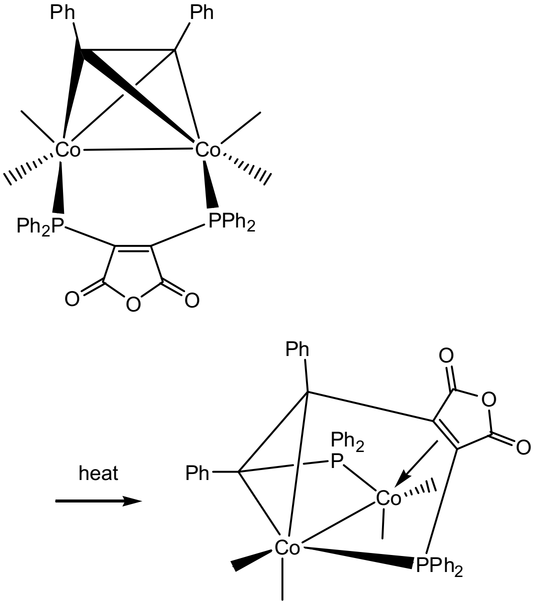
anhydride ligand. These reactions are depicted in Eqs. (1) and (2), respectively.



(1)



(2)

Wishing to further explore the chemistry of our zwitterionic hydrocarbyl complexes, we have investigated the substitution reactivity of $Co_2(CO)_4[\mu\text{-}PhC{=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (**1**) with PMe_3 [5]. The addition of PMe_3 to **1** is shown to trigger the insertion of a CO group into one of the Co–C(hydrocarbyl) bonds to give the acyl species $Co_2(CO)_3(PMe_3)[\mu\text{-}PhC(CO){=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (**2**). Compound **2** undergoes a formal CO deinsertion upon thermolysis to afford the simple PMe_3-substituted derivative $Co_2(CO)_3(PMe_3)[\mu\text{-}PhC{=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (**3**). The course of these substitution reactions has been established through NMR spectroscopy and X-ray crystallographic analyses of compounds **2** and **3**.

2. Experimental

2.1. General

The starting dicobalt compound $Co_2(CO)_4[\mu\text{-}PhC{=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ was prepared from $Co_2(CO)_6(\mu\text{-}PhCCH)$ and bma accordingly to the published procedure [2]. The alkyne compound $Co_2(CO)_6(\mu\text{-}PhCCH)$ was synthesized from $Co_2(CO)_8$ and phenylacetylene [6], while the diphosphine ligand bma was synthesized from 2,3-dichloromaleic anhydride and Ph_2PSiMe_3 [7]. PMe_3 was prepared from $P(OPh)_3$ and MeMgI [8]. The chemicals phenylacetylene, $P(OPh)_3$, and MeI were purchased from Aldrich Chemical Co. and used as received. $Co_2(CO)_8$ was purchased from Strem Chemicals and stored under CO and in the refrigerator when not in use. The ^{13}CO (99%) used in the preparation of the ^{13}C-enriched sample of $Co_2(CO)_6(\mu\text{-}PhCCH)$ was obtained from Isotec. All reaction and NMR solvents were distilled from an appropriate drying agent using Schlenk techniques and stored under argon in storage vessels equipped with high-vacuum Teflon stopcocks [9]. The combustion analyses were performed by Atlantic Microlab, Norcross, GA.

The IR spectral data were recorded on a Nicolet 20 SXB FT-IR spectrometer in sealed 0.1 mm NaCl cells, while the ^{13}C spectral data were recorded at 50 MHz on a Varian Gemini-200 spectrometer. The ^{31}P NMR spectra were collected in the proton-decoupled mode on a Varian 300-VXR spectrometer at 121 MHz, with the reported chemical shifts referenced to external H_3PO_4 (85%), taken to have $\delta = 0$.

2.2. Synthesis of $Co_2(CO)_3(PMe_3)[\mu\text{-}PhC(CO){=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (2)

To a small Schlenk tube containing 0.20 g (0.20 mmol) of **1** in 15 mL of CH_2Cl_2 at room temperature was added 1.05 equiv. of PMe_3 (0.42 mL of a 0.5 M solution of PMe_3 in CH_2Cl_2). The reaction was instantaneous based on TLC and IR analyses of the reaction solution, which revealed the complete consumption of **1** and the formation of **2**. The solvent was removed under vacuum and the residue was passed across a short column of silica gel using CH_2Cl_2/acetone (95:5) as the eluent. Recrystallization of crude **2** from CH_2Cl_2/heptane afforded the analytical sample and single crystals of **2** suitable for X-ray diffraction analysis. Yield of black-green **2**: 0.18 g (85%). IR (CH_2Cl_2): ν(CO) 2022 (vs), 1985 (vs), 1777 (m, symm anhydride), 1719 (m, antisymm anhydride), 1590 (bw, acyl) cm^{-1}. ^{13}C NMR (THF, 178 K): δ 197.83 (d, 1C, $J_{P\text{–}C} = 23$ Hz), 206.65 (s, 2C), 234.50 (d, 1C, $J_{P\text{–}C} = 15$ Hz). ^{31}P NMR (THF, 178 K): δ 14.90 (overlapping resonances, 2P), 19.21 (d, 1P, $J_{P\text{–}P} = 61$ Hz, phosphonium moiety). *Anal.* Calc. for $C_{43}H_{35}Co_2O_7P_3$: C, 59.06; H, 4.03. Found: C, 59.36; H, 4.38%.

2.3. Thermolysis of $Co_2(CO)_3(PMe_3)[\mu\text{-}PhC(CO){=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ and formation of $Co_2(CO)_3(PMe_3)[\mu\text{-}PhC{=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (*3*)

To a Schlenk tube under argon was charged 0.20 g (0.23 mmol) of **2**, followed by the addition of 20 mL of 1,2-dichloroethane (DCE) via syringe. The vessel was sealed and then heated at 60 °C for 1 h, at which time TLC analysis confirmed the presence of compounds **1**, **2**, and **3**. Heating was continued for another hour and the solution examined again by TLC. At this point, only compounds **1** (minor) and **3** (major) were observed ($R_f = 0.80$ for **1** and $R_f = 0.65$ for **3** using CH_2Cl_2 as the eluent). The desired compound **3** was isolated after solvent removal and purification by column chromatography over silica gel using CH_2Cl_2 as the mobile phase. Crude **3** was subsequently recrystallized from CH_2Cl_2/hexane to furnish the combustion sample and the single crystals of **3** suitable for X-ray crystallography. Yield of **3**: 82% (0.16 g). IR (CH_2Cl_2): ν(CO) 2001 (s), 1958 (s), 1777 (m, symm anhydride), 1721 (m, antisymm anhydride) cm^{-1}. ^{13}C NMR (THF, 178 K): δ 202.07 (d, 1C, $J_{P-C} = 20$ Hz), 207.37 (d, 1C, $J_{P-C} = 21$ Hz), 211.89 (s, 1C). ^{31}P NMR (THF, 178 K): δ 10.80 (overlapping resonances, 2P), 33.78 (d, 1P, $J_{P-P} = 67$ Hz, phosphonium moiety). *Anal.* Calc. for for $C_{42}H_{35}Co_2O_6P_3$: C, 59.59; H, 4.13. Found: C, 59.29; H, 4.26%.

2.4. X-ray diffraction data

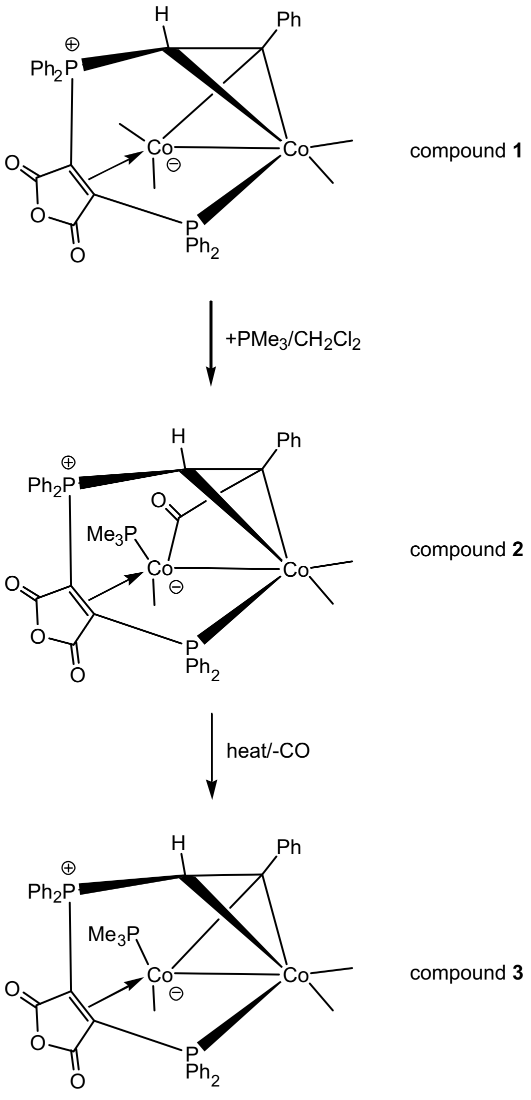
Tables 1 and 2 contain the X-ray data and processing parameters and selected bond distances and angles, respectively, for compounds **2** and **3**. A suitable crystal was selected and sealed inside a Lindemann capillary, followed by mounting on an Enraf-Nonius CAD-4 diffractometer. After the cell constants were obtained, intensity data in the range of 2° ⩽ 2θ ⩽ 44° (**2**) and 2° ⩽ 2θ ⩽ 40° (**3**) were collected at 298 K and were corrected for Lorentz, polarization, and absorption (DIFABS). The structures of compounds **2** and **3** were solved using SHELX-86. All non-hydrogen atoms were located with difference Fourier maps and full-matrix least-squares refinement in both compounds. In the case of **2**, the cobalt, phosphorus, oxygen, and the carbonyl carbon atoms were refined anisotropically, with the phenyl, hydrocarbyl, and maleic anhydride ring carbon atoms refined isotropically. Due to the poor scattering displayed by the crystal of **3**, only the Co and P atoms were refined anisotropically. All hydrogen atoms were assigned calculated positions and allowed to ride on the attached heavy atom. Refinement on **2** converged at $R = 0.0427$ and $R_w = 0.0460$ for 2127 unique reflections

Table 1
X-ray crystallographic data and processing parameters for the dicobalt compounds **2** and **3**

Compound	2	3
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a (Å)	10.2936(7)	9.189(3)
b (Å)	17.471(1)	19.254(4)
c (Å)	22.294(2)	21.702(4)
β (°)		92.00(2)
V (Å^3)	4009.3(5)	3837(2)
Molecular formula	$C_{43}H_{35}Co_2O_7P_3$	$C_{42}H_{35}Co_2O_6P_3$
Fw	874.54	846.53
Formula units per cell (Z)	4	4
D_{calc} (g/mm^3)	1.449	1.465
λ (Mo Kα), Å	0.71073	0.71073
μ (cm^{-1})	9.91	10.32
R_{merge}	n/a	0.037
Absorption correction	Fourier	Fourier
Absorption correction factor	0.90/1.13	0.69/1.32
Total reflections	2811	4000
Independent reflections	2127	1375
Data/residual/parameters	2127/0/301	1375/0/238
R	0.0427	0.0620
R_w	0.0460	0.0715
Goodness of fit on F^2	0.76	0.72
$\Delta\rho$(maximum), $\Delta\rho$(minimum) (e/Å^{-3})	0.45 near Co(1)	0.52 near C(2)

Table 2
Selected bond distances (Å) and angles (°) in the dicobalt compounds **2** and **3**

Compound 2			
Bond distances			
Co(1)–Co(2)	2.650(2)	Co(1)–P(1)	2.187(3)
Co(1)–C(1)	1.77(1)	Co(1)–C(2)	1.79(1)
Co(1)–C(16)	2.030(9)	Co(1)–C(17)	2.022(9)
Co(2)–P(3)	2.239(3)	Co(2)–C(3)	1.73(1)
Co(2)–C(4)	1.944(9)	Co(2)–C(11)	2.095(9)
Co(2)–C(15)	2.006(9)	P(2)–C(15)	1.776(9)
O(4)–C(4)	1.23(1)	C(4)–C(17)	1.48(1)
C(11)–C(12)	1.44(1)	C(11)–C(15)	1.47(1)
C(14)–C(15)	1.47(1)	C(16)–C(17)	1.43(1)
Bond angles			
Co(2)–Co(1)–P(1)	70.08(8)	Co(2)–Co(1)–C(1)	91.8(3)
Co(2)–Co(1)–C(2)	173.1(3)	Co(2)–Co(1)–C(16)	83.7(3)
Co(2)–Co(1)–C(17)	75.2(3)	C(16)–Co(1)–C(17)	41.5(4)
Co(1)–Co(2)–P(3)	159.7(1)	Co(1)–Co(2)–C(3)	93.1(4)
Co(1)–Co(2)–C(4)	65.7(3)	Co(1)–Co(2)–C(11)	81.8(3)
Co(1)–Co(2)–C(15)	89.5(3)	C(4)–Co(2)–C(11)	135.2(4)
C(4)–Co(2)–C(15)	105.3(4)	C(11)–Co(2)–C(15)	41.9(4)
Co(2)–C(4)–O(4)	123.7(7)	Co(2)–C(4)–C(17)	114.7(6)
P(2)–C(16)–C(17)	124.5(7)		
Compound 3			
Bond distances			
Co(1)–Co(2)	2.553(4)	Co(1)–P(1)	2.197(6)
Co(1)–C(1)	1.80(2)	Co(1)–C(2)	1.69(3)
Co(1)–C(16)	2.09(2)	Co(1)–C(17)	1.98(2)
Co(2)–P(3)	2.210(6)	Co(2)–C(3)	1.74(2)
Co(2)–C(11)	2.05(2)	Co(2)–C(15)	2.06(2)
Co(2)–C(17)	2.00(2)	C(11)–C(12)	1.43(3)
C(11)–C(15)	1.39(3)	C(14)–C(15)	1.47(3)
C(16)–C(17)	1.40(3)		
Bond angles			
Co(2)–Co(1)–P(1)	70.9(2)	Co(2)–Co(1)–C(1)	101.5(8)
Co(2)–Co(1)–C(2)	164.6(9)	Co(2)–Co(1)–C(16)	75.2(6)
Co(2)–Co(1)–C(17)	50.4(5)	C(16)–Co(1)–C(17)	40.1(7)
Co(1)–Co(2)–P(3)	154.0(2)	Co(1)–Co(2)–C(3)	92.6(7)
Co(1)–Co(2)–C(11)	84.8(5)	Co(1)–Co(2)–C(15)	89.0(5)
Co(1)–Co(2)–C(17)	49.6(4)	C(11)–Co(2)–C(15)	39.5(7)



Scheme 1.

with $I > 3\sigma(I)$, while **3** afforded convergence values of $R = 0.0620$ and $R_w = 0.0715$ for 1375 unique reflections with $I > 3\sigma(I)$.

3. Results and discussion

3.1. Synthesis, spectroscopic data, and X-ray diffraction structure of 2

Treatment of **1** with a slight excess of PMe_3 at room temperature leads to a rapid reaction based on the brown to black-green color change exhibited by the reaction solution. TLC examination confirmed the complete consumption of brown **1** and the presence of a slower moving black-green spot corresponding to **2** at $R_f = 0.50$ using CH_2Cl_2/acetone (95:5) as the eluent. No reaction between **1** and PMe_3 was observed at 0 °C, while the reaction between **1** and PPh_3 conducted at room temperature showed no sign for the formation of any product. This latter observation suggests that the CO insertion reaction that affords **2** is sensitive to the nucleophilicity of incoming ligand and does not proceed via a pre-equilibrium involving the unsaturated acyl species $Co_2(CO)_3[\mu\text{-}PhC(CO){=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$, as added phosphine would be captured without complications under these circumstances. Compound **2** was subsequently isolated in high yield as a mildly air-sensitive solid after chromatographic separation over silica using the aforementioned eluent. Scheme 1 depicts the transformation of **1** to **2**.

Compound **2** was characterized by IR and NMR spectroscopies, elemental analysis, and X-ray crystallography. The IR spectrum displays terminal Co–CO bands 2022 (vs) and 1985 (vs) cm^{-1} and two ν(CO) bands for the kinematically coupled carbonyl groups associated with the anhydride ring at 1777 (m) and 1719 (m) cm^{-1} [10]. The shift to lower energy by both sets of carbonyl groups in **2** relative to **1** is consistent with the addition of an electron-rich PMe_3 ligand to **1**. The acyl band in **2** appears as a broad, weak band at 1590 cm^{-1}, in agreement with the reported frequencies in other such acyl derivatives [11]. The low-temperature ^{13}C NMR spectrum of a ^{13}CO-enriched sample of **2** exhibits two terminal Co–CO resonances at δ 197.83 (1C) and 206.65 (2C) and an acyl CO resonance at δ 234.50 [12], while the ^{31}P NMR spectrum reveals an overlapping singlet and doublet at δ 14.90 for the cobalt-bound phosphine groups and a down-field doublet at δ 19.21 belonging to the phosphonium moiety. The ^{31}P NMR data recorded for **2** parallel those data reported by us for compound **1**, which displays ^{31}P chemical shifts at δ 4.70 and 31.30 for the phosphine and phosphonium groups, respectively [2].

The solid-state structure of **2** was determined by single-crystal X-ray diffraction analysis [13].[1] Single crystals of **2** exist as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts. The ORTEP diagram of **1**, shown in Fig. 1, confirms the regiospecific addition of the PMe_3 ligand to the Co(2) atom and the insertion of the C(4)O(4) carbonyl group into the Co(2)–C(17) bond of **1**. The Co(1)–Co(2) bond distance of 2.650(2) Å is 0.101 Å longer than the cobalt–cobalt bond length reported for compound **1**. This lengthening is attributed to the presence of the ancillary PMe_3 ligand. The Co(1)–P(1) and Co(2)–P(3) distances of 2.187(3) Å and 2.239(3) Å, respectively, fall within acceptable ranges for such linkages [14]. The Co(2)–C(4) and C(4)–C(17) distances of 1.944(9) Å and 1.48(1) Å, respectively, and the angles associated with the Co(2)–C(4)–C(17) [114.7(6)°] and Co(2)–C(4)–O(4) [123.7(7)°] linkages exhibit values consistent with other acyl-substituted cobalt compounds

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[1] The chiral space group $P2_12_12_1$ exhibited by compound **2** presumably reflects a spontaneous separation of one of the enantiomers from the bulk sample whose composition consists of a racemic mixture of **2**. Unfortunately, the absolute chirality associated with the two stereocenters in the X-ray structure **2** cannot be definitively ascertained based on the available X-ray data.

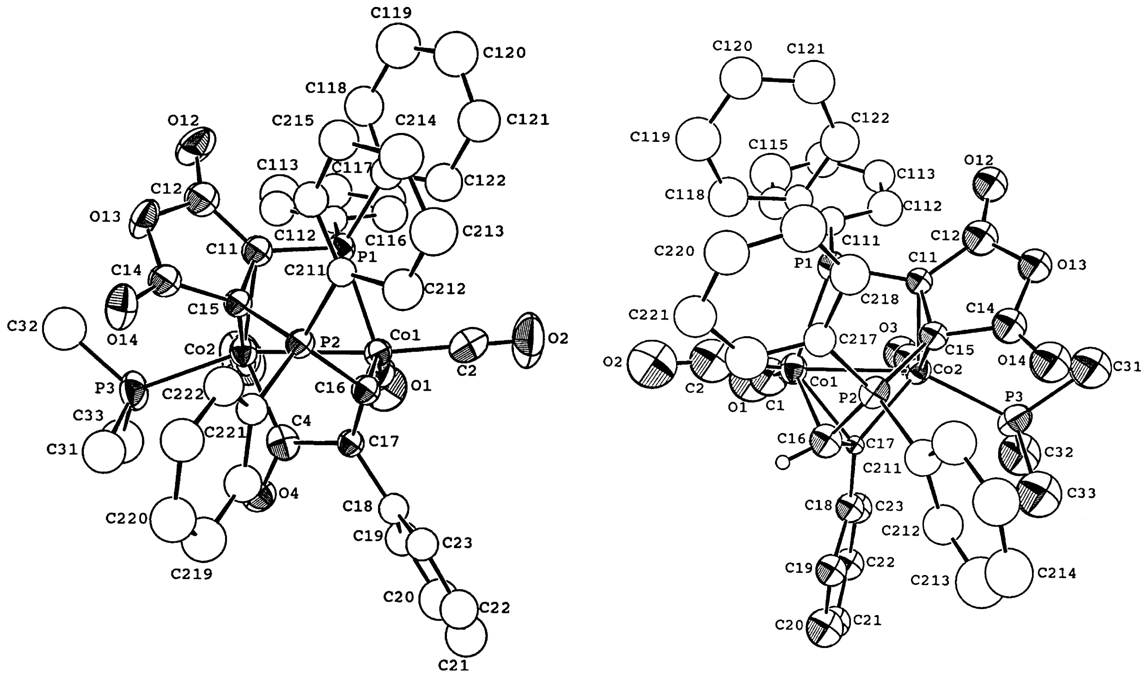

Fig. 1. ORTEP diagrams of compounds **2** (left) and **3** (right) showing the thermal ellipsoids at the 30% probability level.

[15]. The three terminal CO groups display distances and angles consistent with such groups. The remaining bond distances and angles are unremarkable and require no comment.

3.2. Synthesis, spectroscopic data, and X-ray diffraction structure of 3

The temperature sensitivity of **2** was subsequently verified during a routine thermolysis study. Heating **2** in either DCE or toluene solution over the temperature range of 50–75 °C leads to the consumption of **2** and concurrent formation of the simple phosphine-substituted compound **3** as the major product, as assessed by TLC and IR analyses. TLC examination also revealed the presence of a small amount of compound **1** and some decomposed material that remained irreversibly bound to the TLC plate irrespective of the mobile phase employed. The observation of **1** during the thermolysis reaction raises an interesting aspect concerning the route leading to **3**. It is possible that **1** serves as the principal product from the acyl-deinsertion reaction, which in turn requires the expulsion of the PMe_3 ligand from **2**. Once regenerated **1** could again react with the liberated PMe_3 to furnish **2** and then ultimately produce **3** through a slower secondary event(s). The observation of both **1** and **3** from **2** is also consistent with a dual reaction manifold, where the amount of each product (**1** and **3**) reflects a kinetic preference associated with the acyl-deinsertion step [16]. Of these two general paths, we favor the latter one based on the results obtained from the thermolysis of a toluene solution of **2** that was purged with argon in order to remove the liberated CO and PMe_3. Under such conditions, the back reaction between **1** and PMe_3 would be eliminated. Accordingly, **1** would be observed as the dominant product, provided that the expulsion of PMe_3 from **2** is favored over CO dissociation. The significant amount of **3** that accompanies this particular experiment (TLC monitoring) indicates that the conversion of **2** to **3** proceeds primarily through the liberation of CO and not PMe_3. The bottom portion of Scheme 1 shows the conversion of **2** to **3**.

Compound **3** was isolated by column chromatography in 82% yield and characterized by traditional spectroscopic methods, combustion analysis, and X-ray crystallography. The IR spectrum of **3** showed two strong carbonyl stretching bands at 2001 and 1958 cm^{-1} belonging to the terminal Co–CO groups and two anhydride carbonyl bands at 1777 (m) and 1721 (m) cm^{-1} that represent the vibrationally coupled symmetric and antisymmetric anhydride stretches, respectively. The presence of three terminal Co–CO groups in **3** was verified by ^{13}C NMR spectroscopy of a ^{13}CO-enriched sample of **3**. Here, ^{13}C resonances recorded at δ 202.07, 207.37, and 211.89 support the formulated structure of **3** and the loss of the acyl moiety. The ^{31}P NMR spectrum of **3** exhibits a high-field resonance at δ 10.80 for the overlapping cobalt-bound phosphine moieties and the hydrocarbyl-bound phosphonium ligand at δ 33.78. These data are similar to those chemical shifts recorded for compound **2**.

The molecular composition of **3** was established by X-ray diffraction analysis. The ORTEP diagram of **3** depicted in the right-hand portion of Fig. 1 confirms the loss of the acyl moiety in the conversion of **2** to **3**. With the exception of the ancillary PMe_3 group at Co(2), the overall structure of **3** is comparable to the published structure of **1** [2]. The 2.553(4) Å bond distance for the Co(1)–Co(2) vector is in keeping with its single-bond designation and consistent with those Co–Co bond lengths found in other dinuclear cobalt compounds [17]. The cobalt-bound alkene moieties defined by the atoms C(11)–C(15) and C(16)–C(17) exhibit bond distances of 1.39(3) and 1.40(3) Å, respectively, that are slightly shorter than those distances found in **2**. The remaining bond distances and angles are unexceptional and require no comment.

4. Conclusions

The addition of PMe_3 to $Co_2(CO)_4[\mu\text{-PhC}{=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (**1**) promotes the regiospecific CO insertion into one of the Co-C(hydrocarbyl) bonds and production of the acyl compound $Co_2(CO)_3(PMe_3)[\mu\text{-PhC(CO)}{=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (**2**). This represents the first example of a phosphine-induced CO-insertion reaction in a zwitterionic hydrocarbyl compound of this genre. Compound **2** is thermally unstable and undergoes decarbonylation to furnish the PMe_3-substituted compound $Co_2(CO)_3(PMe_3)[\mu\text{-PhC}{=}C(H)PPh_2C{=}C(PPh_2)C(O)OC(O)]$ (**3**) and **1**, as the major and minor products, respectively. Our future endeavors will explore the generality of this reaction with isonitrile ligands and different phosphines, and the kinetics for the CO insertion reaction will be investigated using low-temperature spectroscopic techniques.

Acknowledgement

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Appendix A. Supplementary material

CCDC 627411 and 627412 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.04.004.

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