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Structure of $Co_2(CO)_6(dppm)$ and $Co_2(CO)_5(CHCO_2Et)(dppm)$ (dppm = $Ph_2PCH_2PPh_2$) and exchange reaction with ¹³CO: An experimental and computational study

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Abstract

Crystal structures of Co₂(CO)₆(dppm) (1) and Co₂(CO)₅(CHCO₂Et)(dppm) (2) (dppm = Ph₂PCH₂PPh₂) show asymmetry with respect to the orientation of the phenyl groups in 1 and owing to the bridging ethoxycarbonylcarbene ligand in 2. The effect of this asymmetry was recognized in the solid-state ³¹P NMR spectra of 1 and 2 and in the solid-state and solution ¹³C NMR spectra of 2 as well, but not in the solid-state and solution ¹³C NMR spectra of 1. In CH₂Cl₂ solution under an atmosphere of ¹³CO, the CO ligands of both complexes exchange with ¹³CO. The overall rate of ¹³CO exchange at 10 °C was found to be $k_{obs} = 0.107 \times 10^{-3} \text{ s}^{-1}$ for 1 and $k_{obs} = 0.243 \times 10^{-3} \text{ s}^{-1}$ for 2. Two-layered ONIOM(B3LYP/6-31G(d):LSDA/LANL2MB) studies revealed fluxional behavior of 1 with rather small barriers of activation of the rearrangements. Four possible isomers have been computed for 2, close to each other energetically.

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1. Introduction

The cobalt complex $Co_2(CO)_6(dppm)$ (1) is smoothly formed from $Co_2(CO)_8$ and dppm (dppm = Ph₂PCH₂PPh₂) in benzene [1] or CH₂Cl₂ solution [2,3] (Eq. (1)).

$$\operatorname{Co}_{2}(\operatorname{CO})_{8} + \operatorname{dppm} \xrightarrow[C_{6}H_{6} \text{ or } \operatorname{CH}_{2}\operatorname{Cl}_{2}]{2} \operatorname{Co}_{2}(\operatorname{CO})_{6}(\operatorname{dppm}) + 2\operatorname{CO}_{1}$$
(1)

The structure of complex **1** has been assumed [2] to be analogous to that of $\text{Co}_2(\text{CO})_6\text{L}$ (L = μ -[1,2-bis(dimethylarsino) tetrafluorocyclobutene-AsAs]) [4,5], which was confirmed recently by an X-ray crystal structure determination [6].

Obviously the depiction of complex 1 as having a symmetrical structure [2,3,7], where a plane formed by the two cobalt and the PCH₂P fragment bisecting the planes of the two bridging carbonyls, is wrong.

Complex 1 was reported to give in the dediazotation reaction of ethyl diazoacetate complex 2 (Eq. (2)) in which reaction one of the bridging carbonyl of 1 is replaced by an ethoxycarbonylcarbene unit.

$$1 + \text{EtO}_2\text{CCHN}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\Delta} Co_2(\text{CO})_5(\text{CHCO}_2\text{Et})(\text{dppm}) + \text{CO} + \text{N}_2$$
(2)

Based on the large three-bond ${}^{3}J(PH)$ coupling of the μ -alkylidene resonance in the low-temperature ${}^{1}H$ NMR spectra of **2** (δ 4.64, J(PH) 21 Hz) a Newman projection of the structure of complex **2** was proposed [8] (see Scheme 1).

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Complex 1 was found to be a suitable catalyst for the carbonylation of ethyl diazoacetate in the presence of ethanol to give diethyl malonate product [9] (Eq. (3)).

$$EtO_{2}CCHN_{2} + CO + EtOH \xrightarrow{2 \text{ mol } \% \text{ I}}_{50 \text{ bar},45 \circ \text{C},4 \text{ d}} EtO_{2}CCH_{2}CO_{2}Et + N_{2}$$
(3)

Complex **2** is probably involved in the catalytic cycle (see Scheme 2) since both its formation from **1** and ethyl diazo-acetate [8] and the reaction of complex **2** with carbon monoxide and ethanol [10] were demonstrated.

We report here the results of various solid-state and solution spectroscopic investigations of 1 and 2 and the results of an X-ray structure determination of 2. The results indicate the non-equivalence of the phosphorus atoms in the complexes. In addition we studied the exchange reactions of 1 and 2 with ¹³CO in methylene chloride solution. Structures and possible transition states of the exchange reactions were computed.

2. Experimental

All operations were performed under exclusion of air and moisture using the usual Schlenk technique [11]. IR spectra were recorded with a Thermo Nicolet Avatar 330 FTIR spectrometer in KBr pellets or using 0.00765, 0.02095, or 0.05097 cm CaF₂ solution cells, calibrated by the interference method [12]. Both the liquid-phase and the solid-state NMR experiments were performed on a Bruker Avance 400 NMR spectrometer equipped with a 5 mm broad-band variable temperature liquid and a 4 mm variable temperature MAS probe. The solutionphase spectra were recorded in CDCl₃ at room temperature or in CD₂Cl₂ at 200 K. Approximately 5-30 mg samples were used for the solution studies. The ¹³C and ³¹P resonance frequencies, $\omega_0/2\pi$ were -100.613and -161.976 MHz, respectively. The MAS spectra were recorded with high-power (~100 W) proton decoupling. Sample spinning speeds were typically varied between 10000 and 12500 \pm 1 Hz. 90–100 mg sample quantities were used in 4 mm o.d. zirconia or Si_3N_4 rotors. The number of scans varied between 32 and 128 for the ³¹P spectra and 1500–2500 for the ¹³C spectra. For phosphorus both MAS (with recycling delays of 12-15 s) and CP/MAS spectra (with contact times of 0.7–1.5 ms and recycling delays of 6 s) were recorded and gave practically identical results. The ¹³C chemical shifts are referred to external TMS







 $(\delta_{\rm CDCl3} = 77 \text{ ppm}$ was used for the conversion). For solid-state work for referencing and set-up purposes polycrystalline glycine was used ($\delta_{\rm iso} = 176.5 \text{ ppm}$ (α -polymorph) relative to TMS) by the substitution method. In case of ³¹P 90° the pulse width was about 3.6 µs. For referencing and set-up purposes, polycrystalline PPh₃ was applied ($\delta_{\rm iso} = -6 \text{ ppm}$ relative to the 85% H₃PO₄) by the substitution method. ¹³CO (99% isotope purity) was obtained from Sigma–Aldrich.

X-ray crystal structure determination. Intensity data collections were performed on a Rigaku R-axis Rapid IP diffractometer at ambient temperature with MoKa radiation ($\lambda = 0.7107$ Å). The structure was solved by direct methods [13] and refined by full matrix least-squares [14] against F^2 . A survey [15] showed that a fraction of non-centrosymmetric crystal structures published in Inorg. Chim. Acta are in fact centrosymmetric. Compound 2 was treated as a racemic twin and the absolute structure parameter (at 97.5% Friedel pair coverage) is 0.510(18), typical of a centrosymmetric structure. The structure indeed, can be solved in space group *Pbca* but it is non-refinable (R = 0.1275, $wR_2 = 0.4647$, with unusual ADP ellipsoids in the phenyl rings). Therefore the Pca21 space group was retained. Complex 2 also contains unidentifiable solvent molecule(s). The SQUEEZE procedure [16] was applied to eliminate these atoms (volume of solvent accessible area: 1041.0 Å^3 , electron count: 59/cell). Crystal data, data collection and refinement parameters are listed in Table 1.

2.1. Preparation of $Co_2(CO)_6(dppm)$ (1)

The preparation of $\text{Co}_2(\text{CO})_6(\text{dppm})$ followed published procedures [1–3]. Analytically pure **1** was obtained by slow diffusion of *n*-pentane into a solution of **1** in CH₂Cl₂ (120 mg/cm³) at 5 °C. IR (KBr pellets) v(C=O) 2042, 1998, 1982, 1971 cm⁻¹, v(C=O) 1809, 1797 cm⁻¹, IR (CH₂Cl₂) v(C=O) 2045 ($\varepsilon_{\text{M}} = 2808 \text{ cm}^2/\text{nmol}$), 2012 ($\varepsilon_{\text{M}} = 3406 \text{ cm}^2/\text{nmol}$), 1985 ($\varepsilon_{\text{M}} = 3751 \text{ cm}^2/\text{nmol}$) cm⁻¹, v(C=O) 1820 ($\varepsilon_{\text{M}} = 823 \text{ cm}^2/\text{nmol}$), 1794 ($\varepsilon_{\text{M}} = 1066 \text{ cm}^2/\text{nmol}$) cm⁻¹, ¹³C NMR (293 K, CDCl₃): δ 216.3 ppm (terminal and bridging carbonyls, in fast exchange); 134.3 ppm (*ipso* carbons, pseudo triplet); 131.8 ppm (*meta* carbons, pseudo triplet); 130.4 ppm (*para* carbons, singlet); 128.6 ppm (*ortho* carbons, pseudo triplet); 29.4 ppm (P–CH₂–P carbons, pseudo triplet). ³¹P Table 1

Crystal data and structure refinement of Co₂(CO)₅(CHCO₂Et)(dppm) (2)

| Empirical formula | C ₃₄ H ₂₈ Co ₂ O ₇ P ₂ |
|---|---|
| Formula weight | 728.36 |
| Temperature (K) | 293(2) |
| Crystal system | orthorhombic |
| Space group | $Pca2_1$ |
| a (Å) | 18.235(3) |
| b (Å) | 18.121(4) |
| c (Å) | 21.843(4) |
| β (°) | |
| Volume (Å ³) | 7218(2) |
| Ζ | 8 |
| D_{calc} (Mg/m ³) | 1.340 |
| Absorption coefficient, μ (mm ⁻¹) | 1.052 |
| <i>F</i> (000) | 2976 |
| Crystal size (mm) | $0.529 \times 0.516 \times 0.482$ |
| Absorption correction | multi-scan |
| Maximum/minimum transmission | 0.600/0.520 |
| θ -Range for data collection (°) | $3.12 \leqslant \theta \leqslant 27.48$ |
| Reflections collected | 58096 |
| Independent reflections [R(int)] | 16329 [0.0548] |
| Reflections $I > 2\sigma(I)$ | 13053 |
| Data/restraints/parameters | 16329/1/811 |
| Goodness-of-fit on F^2 | 1.052 |
| Final <i>R</i> indices $[I \ge 2\sigma(I)]$ | $R_1 = 0.0571, wR_2 = 0.1397$ |
| R indices (all data) | $R_1 = 0.0732, wR_2 = 0.1482$ |
| Maximum and mean shift/e.s.d. | 0.005; 0.001 |
| Largest difference in peak/hole (e $Å^{-3}$) | 0.836 and -0.528 |

NMR (293 K, CDCl₃): δ 60.8 (s) ppm, ³¹P NMR (200 K, CD₂Cl₂): δ 62.3 (s) ppm.

¹³C SS-NMR (293 K, polycrystalline sample): 134.2– 121 ppm (phenyl carbons, not sufficiently resolved); 27.4 ppm (P–CH₂–P). ³¹P SS-NMR (293 K, polycrystalline sample): $\delta \sim 63.5$ (m) and ~ 59.6 ppm (m).

2.2. Preparation of $Co_2(CO)_5(CHCO_2Et)(dppm)$ (2)

To a solution of $Co_2(CO)_6(dppm)$ (1) (268 mg, 0.40 mmol) in CH_2Cl_2 (7.8 cm³) ethyl diazoacetate (50.2 mg, 0.44 mmol) was added and refluxed for 2.5 h. Progress of the reaction was followed by IR (disappearance of the $v(N \equiv N)$ band of ethyl diazoacetate at 2112 $(\varepsilon_{\rm M} = 800 \text{ cm}^2/\text{mmol}) \text{ cm}^{-1})$, and by TLC on Silica gel/ CH₂Cl₂: by disappearance of complex 1, $R_{\rm f}(1) = 0.785$, $R_{\rm f}(2) = 0.354$. By removing the solvent in vacuum below 0 °C complex 2 was obtained as red crystalline solid (295 mg, 0.39 mmol, 97.5% yield). Analytically pure 2 suitable for a single-crystal structure determination was obtained by slow diffusion of *n*-pentane into a solution of 2 in CH_2Cl_2 (120 mg/cm³) at 5 °C. IR (KBr pellets) $v(C \equiv O)$ 2044, 2010, 1987 cm⁻¹, $v(C \equiv O)$ 1813, $v(C \equiv O)_{\text{org.}}$ 1677 cm⁻¹, IR (CH₂Cl₂) $v(C \equiv O)$ 2045 ($\varepsilon_{\text{M}} = 2953 \text{ cm}^2/$ mmol), 2015 ($\epsilon_{\rm M} = 4001 \text{ cm}^2/\text{mmol}$), 1989 ($\epsilon_{\rm M} = 3358 \text{ cm}^2/\text{mmol}$) cm⁻¹, v(C=O) 1822 ($\epsilon_{\rm M} = 946 \text{ cm}^2/$ mmol) cm⁻¹, $v(C=O)_{org.}$ 1689 ($\varepsilon_{M} = 204 \text{ cm}^{2}/\text{mmol}$), 1650 ($\varepsilon_{M} = 230 \text{ cm}^{2}/\text{mmol}$) cm⁻¹. ¹H NMR: (303 K, CDCl₃): δ 1.23 (t, 3H, CH₃), 2.6 (dt, 1H, H_B, $J_{AB} = 14$ Hz,

 $J_{\rm PCHB} = 7-8$ Hz), 3.16 (dt, 1H, H_A, $J_{\rm AB} = 14$ Hz, $J_{\text{PCHA}} = 10 \text{ Hz}$, 4.06 (q, 2H, CH₃CH₂), 4.53 (t, 1H, $J_{\text{PCHmethin}} = 21.5 \text{ Hz}$, 7.2–7.7 (m, 10H, Ph-H). ¹³C NMR: (293 K, CDCl₃): $\delta \sim 239.0$ ppm (bridging carbonyl); 205.2 and 202.7 ppm (terminal carbonyls); 181.3 ppm (-C = 0)O-carbonyl); 136.4 and 134.5 ppm (*ipso* phenyl) carbons, pseudo triplets); 132.6 and 131.0 ppm (ortho phenyl carbons, poorly resolved pseudo triplets); 130.4 and 130.0 ppm (para phenyl carbons, singlets); 128.6 ppm (meta phenyl carbons, poorly resolved pseudo triplet); 94.5 ppm (bridging -CH-carbon); 60.0 ppm (-O- CH_{2-}); 53.4 ppm (CH₂Cl₂); 27.3 ppm (P-CH₂-P, triplet); 14.2 ppm (-CH₃). ³¹P NMR (293 K, CDCl₃): δ 57.6 (s) ppm, ³¹P NMR (200 K, CD₂Cl₂): δ 58.2 (s) ppm. ¹³C SS-NMR (293 K, polycrystalline sample): $\delta \sim 244.7$ ppm (bridging carbonyls); \sim 204.3 ppm (terminal carbonyls); 181.4 ppm (-C(=O)O); 138.6–124 ppm (phenyl carbons, not sufficiently resolved); ~ 105.4 ppm (bridging -CH-carbon); 59.8 ppm ($-O-CH_2-$); 53.5 ppm (most probably CH_2Cl_2) is present in the crystals); 28.3 ppm ($P-CH_2-P$); 15.6 ppm $(-CH_3)$. ³¹P SS-NMR (293 K, polycrystalline sample): δ \sim 52.3 (m) and 50.2 (m) ppm.

2.3. Reaction of $Co_2(CO)_7(CHCO_2Et)$ with dppm

To a solution of $Co_2(CO)_7(CHCO_2Et)$ [17] (10 mg, 0.025 mmol) in CH_2Cl_2 (2.0 cm³) under argon dppm (9.6 mg, 0.025 mmol) was added at room temperature and stirred for 30 min. In accord with the TLC analysis, the IR spectrum of the reaction mixture at 1822 and 1794 cm⁻¹ showed the presence of a 1:3 mixture of complex 1 and complex 2. Repeating the experiment in the presence of ethanol (0.025 mmol) diethyl malonate (0.007 mmol, 28% yield) was formed beside complexes 1 and 2, according to quantitative infrared analysis, using the molar absorbance of diethyl malonate $\varepsilon_M(CH_2Cl_2)$, 1749 cm⁻¹ = 579 cm²/mmol, and $\varepsilon_M(CH_2Cl_2)$, 1749 cm⁻¹ = 666 cm²/mmol.

2.4. Preparation of ^{13}CO enriched samples of complex 2

To a solution of complex 2 (34.0 mg, 0.045 mmol) in CH_2Cl_2 (0.85 cm³) under argon in a closed Schlenk flask fitted with a silicon-rubber injection port (total inner volume: 12 cm³) ¹³CO (6 cm³) was added using a gas-tight syringe at room temperature. After stirring for an hour, the solvent was removed under vacuum, and the residue dissolved under argon in CH₂Cl₂ (0.85 cm³). After closing the flask a new portion of ¹³CO (6 cm³) was injected and the reaction mixture was stirred for an hour. Repeating this procedure four-times resulted in a 39.4% ¹³CO-enrichment of the carbonyl ligands in complex 2 as could be calculated based on the intensities of the bridging carbonyl bands $v(^{12}C=0)$ at 1822 ($\varepsilon_M = 946 \text{ cm}^2/\text{mmol}$) and $v({}^{13}C=0)$ at 1783 ($\epsilon_M = 909 \text{ cm}^2/\text{mmol}$) cm⁻¹. The ε_{M} of the v(¹³C=O) band was calculated from the experimentally measured ε_{M} value of the $v(^{12}C=0)$ band by

multiplying it with the mass correction value $(12/13)^{-0.5} = 0.96077$.

2.5. Measurement of the rate of ^{13}CO incorporation into complex 1 and 2

For the measurements a magnetically stirred thermostatted glass reactor (35 cm³ total volume) was used, equipped with a gas inlet and with a silicon disk port. The gas inlet was connected through a two-way stopcock to a vacuum pump and a ¹³CO-filled gas burette, respectively. A stainless-steel cannula connected to a 3-port Tvalve was immersed close to the bottom of the reactor through the silicon disk. To the two other ports of the valve a Hamilton TLL syringe $(2.5 \text{ cm}^3 \text{ volumes})$ and the IR cell (through a PTFE tubing) were connected. Samples from the reaction mixture for IR analyses were withdrawn through the stainless steel cannula, and pumped into the IR cell continuously by using the Hamilton TLL syringe, allowing the liquid sample to return from the IR cell to the reactor through a second PTFE tubing. The solvent and the solution of the reactant were added to the ¹³CO-filled reactor through the silicon disk using Hamilton TLL syringes. In typical experiments the reactor and its connected parts were first evacuated and then filled with ¹³CO (740 mm Hg total pressure) and CH_2Cl_2 (6.5 cm³) was added. After stirring at 10 °C for 10 min the reaction was started by injection of a precooled solution of complex 1 or complex 2 (0.066 mmol) in CH₂Cl₂ (1.5 cm^3). Infrared spectra were recorded with four scans after 2, 4, 6, 8, 12, 16, 20, 30,... min, and so on until the ¹³CO enrichment of 30.1% (complex 1) or 44.2% (complex 2) has been reached in ca. 24 or 14 h, respectively. The rate constant of the overall ¹³CO incorporation $(0.107 \times 10^{-3} \text{ s}^{-1} \text{ for}$ complex 1, and 0.243×10^{-3} s⁻¹ for complex 2) was calculated from the initial changes of the concentration of complex 1 or complex 2, as obtained from the intensity values measured at 1820 cm^{-1} (1) or 1822 cm^{-1} (2), or that ofCo₂(13 CO)_x(CO)_{6-x}(dppm) or Co₂(13 CO)_x(CO)_{5-x}-(CHCO₂Et)(dppm) from the intensity values measured at 1758 cm^{-1} (1) or 1783 cm^{-1} (2) by dividing the observed initial rates with the initial concentration of complex 1 or complex 2.

2.6. Computational details

All the structures (minima and transition states) were fully optimized without symmetry constraints within the framework of the density functional theory using the ONI-OM method developed by Morokuma and co-workers [18]. The whole system was divided into two layers. The B3LYP functional [19] was used for the inner layer in combination with the 6-31G(d) basis set [20] while the remainder, containing only the phenyl rings of the dppm ligand, was treated with the local spin density approximation (LSDA) [21,22] utilizing the LANL2MB basis set [23,24]. For all the calculations the GAUSSIAN 03 program package was used [25].

3. Results and discussion

3.1. Crystal structure of 2

The crystal structure of 2 (Fig. 1) shows that the ethoxycarbonylcarbene replaces one of the bridging carbonyls in complex 1, which was closer to the phosphorus atoms. The crystal data and structure refinement, and selected bond lengths and angles are compiled in Tables 1 and 2.

3.2. NMR and IR spectra of 1 and 2

NMR spectra of complexes 1 and 2 show symmetrical structures when recorded in liquid phase. The solution ³¹P NMR spectra of complexes 1 and 2 exhibit singlet absorptions between 200 and 293 K (see Section 2). In the ¹³C NMR spectra all carbon atoms but the carbonyls and the phenyl para carbons (these are not coupled to chemically equivalent but magnetically inequivalent P atoms) show the expected pseudo triplets corresponding to the AXX' spin systems $(A = {}^{13}C, X = X' = {}^{31}P)$ [26]. As an instructive example see the aromatic region of complex 2 (Fig. 2). It proves unambiguously that in this compound two kinds of P-bound phenyl rings can be distinguished at room temperature. While the *ipso* carbons having sizeable P-C coupling exhibit well resolved pseudo triplets, likewise the *meta* and *ortho* carbons exhibit also triplet-like fine structures (though much less resolved due to the different P-C couplings), the para carbons lacking measurable P-C couplings show singlets. Note that there is no plane of symmetry between the CO groups trans to



Fig. 1. Molecular diagram of molecule 1 of the asymmetric unit of complex 2 with the atomic numbering (hydrogen atoms are omitted for clarity).

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s of $Co_2(CO)_5(CH-$

| CO_2Et)(dppm) (2) ^a | | |
|-----------------------------------|------------|--|
| Co(1)–Co(2) | 2.4202(13) | |
| | 2.4268(12) | |
| Co(1)–P(1) | 2.2595(17) | |
| | 2.2405(16) | |
| Co(2)–P(2) | 2.2466(17) | |
| | 2.2559(16) | |
| Co(1)–C(1) | 1.972(7) | |
| | 1.994(7) | |
| Co(1)–C(2) | 1.963(7) | |
| | 1.907(6) | |
| Co(2)–C(1) | 1.965(7) | |
| | 1.966(7) | |
| Co(2)–C(2) | 1.931(6) | |
| | 1.938(6) | |
| P(1)-Co(1)-Co(2) | 97.97(5) | |
| | 98.60(5) | |
| P(2)-Co(2)-Co(1) | 98.16(5) | |
| | 98.06(5) | |
| P(2)–C(7)–P(1) | 113.0(3) | |
| | 113.7(3) | |

^a Numbering of atoms according to Fig. 1.

the P atoms and those of quasi-*trans* to the bridging CH group. On the other hand, in complex 1 all the phenyl and the carbonyl groups are equivalent (see Fig. 3 for the aromatic region of complex 1) indicating fast exchange between the *axial* and *equatorial* and bridging and terminal positions, respectively. Owing to the fluxional behavior of

1, only one set of the two methylene protons was observed [3] in form of a triplet at 3.15 ppm. One of the reviewers pointed out that in contrast to 1 in ¹H NMR of 2, there shall be two sets of multiplets for the two methylene protons, since a back and forth motion around the dicobalt fragment does not average out the differences in their chemical environments. Indeed, we found two sets for those protons as doublets of triplets at 2.6 and 3.16 ppm (see Section 2), supporting this expectation.

The symmetry is lost in solid phase (see Figs. 4 and 5 for the ³¹P and ¹³C CPMAS spectra of **2**, respectively). The ³¹P CPMAS spectra exhibit complicated unsymmetrical multiplets between 65 and 45 ppm. The multiplet structure of the signals observed only in the solid-state is due the residual dipolar coupling existing between the ³¹P and quadrupolar ⁵⁷Co nuclei. Similar cases for the ³¹P(I = 1/2)–⁵⁷Co(I = 7/2) pair have already been reported [27,28]. The fine structure of the signals (two heavily overlapped, distorted octets) can be taken as an unambiguous proof for the direct ³¹P–⁵⁷Co bonds and for the two different ³¹P sites. The isotropic chemical shifts can be estimated from the centre of gravity of the observed transitions.

The ¹³C CPMAS spectrum is even more informative. Based on the same phenomenon signals of carbon atoms attached directly to one or two ⁵⁷Co nuclei show multiplets. Although not all transitions of the octets can be identified the bridging and terminal CO groups and the bridging –CH–carbon atom can be clearly assigned to the signals at 244.7, ~206, and at ~104 ppm, respectively. At the same



Fig. 2. 13 C NMR spectrum of **2** (aromatic region only) recorded in CDCl₃ at room temperature at 9.39 T. The two *meta* carbons overlap accidentally at 128.59 ppm.



Fig. 3. $^{13}\!C$ NMR spectrum of 1 (aromatic region only) recorded in CDCl3 at room temperature at 9.39 T.



Fig. 4. ³¹P CPMAS spectrum of **2** recorded at 9.39 T, spinning speed 12500 Hz, room temperature. The isotropic transitions are indicated by numbers. For clarity only the first pair (+1, -1) of the spinning side band manifold is shown.



Fig. 5. ¹³C CPMAS spectrum of **2** recorded at 9.39 T, spinning speed 12500 Hz, room temperature. The isotropic signals are indicated by numbers. The signal at 53.5 ppm is tentatively assigned to CH₂Cl₂ present in the crystals.

time all other carbons not attached to cobalt atom exhibit singlets (the observed line widths are larger than the one, two or three-bond ${}^{13}C_{-}{}^{31}P$ spin–spin couplings therefore these couplings cannot be seen).

The ³¹P solid-state spectra of complex 1 (not discussed in details) showed similar features, however, in the ¹³C CPMAS spectrum, unlike 2, practically only the protonated carbons gave signals. This can be explained by the lack of protons in vicinity of the carbonyls, but also the exchange of bridging and terminal carbonyls, still going on in the solid-state, can scale down the dipolar interactions responsible to the magnetization transfer.

The solid-state IR spectrum of complex 1 in KBr show four terminal and two bridging carbonyl absorptions in accord with the asymmetric structure revealed by the crystal structure determination and the solid-state NMR spectra. In CH₂Cl₂ solution, however, only three (but broad) terminal carbonyl absorptions were found, indicating a more symmetrical environment for those v(C=O) vibrations. In the case of complex 2 both in the solid-state and in solution three terminal and one bridging carbonyl stretching vibrations were detected.

3.3. An alternative pathway for the preparation of complex **2**

Although the dediazotation reaction (Eq. (2)) of ethyl diazoacetate with $Co_2(CO)_6(dppm)$ offer the best practical way to prepare complex **2** we checked an alternative pathway according to Eq. (4).

$$Co_{2}(CO)_{7}(CHCO_{2}Et) + dppm \xrightarrow{r.t.} Co_{2}(CO)_{5}(CHCO_{2}Et)(dppm) + 2CO$$
(4)

Applying a 1:1 molar ratio of $Co_2(CO)_7(CHCO_2Et)$ and dppm at room temperature in CH_2Cl_2 solution, a 1:3 mixture of $Co_2(CO)_6(dppm)$ and $Co_2(CO)_5(CHCO_2Et)(dppm)$ is formed. Under these reaction conditions 25% of the ethoxycarbonylcarbene ligand from the complexes is lost probably by its diphosphane-induced coupling with carbon monoxide. The highly reactive product of this coupling reaction, ethoxycarbonylketene can be trapped with ethanol in form of diethyl malonate [17].

3.4. ¹³CO exchange experiments

Using ¹³CO atmosphere over solutions of complex 1 in CH₂Cl₂ at 10 °C, incorporation of ¹³CO can be recognized according to Eq. (5) from the beginning of the reaction by the shifts of the v(CO) bands of the coordinated CO ligands of complex 1 to lower wave numbers in the solution infrared spectra. In the terminal v(C=O) range the various v(¹²C=O) and v(¹³C=O) bands are strongly overlapping during the progress of the exchange reaction. In parallel to that, however, one of the bridging v(¹²C=O) bands at 1820 cm⁻¹ and one of the bridging v(¹²C=O) bands at 1758 cm⁻¹ are separated and are suitable for quantitative determination the rate of the exchange reaction. The overall rate of ¹³CO exchange of complex 1 was calculated as

 $k_{\rm obs} = 0.107 \times 10^{-3} \,\text{s}^{-1}$ which is about 56 times less than that found for $\text{Co}_2(\text{CO})_8$ [29 and references therein].

$$\operatorname{Co}_{2}(\operatorname{CO})_{6}(\operatorname{dppm}) + x^{13}\operatorname{CO} \xrightarrow[\operatorname{CH}_{2}\operatorname{Cl}_{2}]{}^{10 \, \circ \mathrm{C}} \operatorname{Co}_{2}(\operatorname{CO})_{6-x}({}^{13}\operatorname{CO})_{x}(\operatorname{dppm}) + x\operatorname{CO}$$
(5)

Under the conditions above, complex **2** behave similarly. Incorporation of ¹³CO can be recognized according to Eq. (6) from the beginning of the reaction by the shifts of the v(CO) bands of the coordinated CO ligands of complex **2** to lower wave numbers in the solution infrared spectra. For quantitative purposes the bridging $v(^{12}C=O)$ band at 1822 cm⁻¹ and the bridging $v(^{13}C=O)$ band at 1783 cm⁻¹ was used to calculate the overall rate of ¹³CO exchange. The overall rate of ¹³CO exchange of complex **2** was calculated as $k_{obs} = 0.243 \times 10^{-3} \text{ s}^{-1}$ which is more than twice of that for complex **1**. This rate is two orders of magnitude slower than that observed under the same conditions for the complex Co₂(CO)₅(CHCO₂Et)(PPh₃)₂ [30].

$$2 + x^{13} \text{CO} \xrightarrow[\text{CH}_2\text{CI}_2]{0 \circ \text{C}} \text{CO}_2(\text{CO})_{5-x} (^{13}\text{CO})_x(\text{CHCO}_2\text{Et}) \times (\text{dppm}) + x\text{CO}$$
(6)

3.5. Computed structures of complexes 1 and 2

The optimized structures of **1** and **2** are depicted in Fig. 6. Both geometries are in reasonable agreement with the corresponding crystal structures, however the orientation of the phenyl rings are somewhat different than in condensed phase. The cobalt–carbonyl carbon bond distances are shorter than those in the analogous $Co_2(CO)_7(\mu$ -CH₂) complexes containing no P-donor ligands [31], thus larger dissociation energies for the Co– $C_{carbonyl}$ bonds are expected. The axial CO ligands are more strongly bound to cobalt than the equatorial ones.

3.6. Isomerization of **1** and CO dissociation in $Co_2(CO)_6(dppm)$ complexes

As discussed in Section 3.1, the NMR spectra of 1 indicated a very fast exchange of the carbonyl groups, similarly to that in $Co_2(CO)_8$, which is generally explained with the very facile interconversion between the double-bridged C_{2v} and the unbridged D_{2d} and D_{3d} structures [32]. For $Co_2(CO)_6(dppm)$ only two isomers have been located (see Fig. 7), namely with a dibridged (1) and a semi-bridged (1a) structure, respectively. The semi-bridged structure is higher in free energy by 4.6 kcal/mol and the barrier of the interconversion is 6.1 kcal/mol.

Dissociation of an equatorial CO from 1 leads to the coordinative unsaturated dibridged complex 3a with the free energy of dissociation of 19.7 kcal/mol. The looser bound equatorial CO in 1a results in a lower free energy of dissociation, namely 14.9 kcal/mol and structure 3b possessing a semi-bridged CO ligand. However, taking into



Fig. 6. Computed structures of 1 and 2 optimized at the ONI-OM(B3LYP:LSDA) level of theory. The hydrogen atoms of the phenyl rings are omitted for clarity.

account the higher thermal stability of 1, the more preferred pathway of the CO dissociation is $1 \rightarrow 3a$, directly.

The coordinative unsaturated **3a** can also readily isomerize to the semi-bridged **3b** via **3abTS** with a free energy of activation of 1.5 kcal/mol (see Fig. 8). Both isomers are almost degenerate energetically, but **3b** is more stable by 0.2 kcal/mol. The other transition state found on the potential energy hyper surface describes the migration of one of the terminal CO ligands from one cobalt to the other via transition state **3aaTS**. The free energy of activation for this process is 5.7 kcal/mol.

The infrared data of the carbonyl complexes containing dppm ligand are collected in Table 3. Since no scaling factor to offset the systematic error caused by neglecting of anharmonicity for the ONIOM(B3LYP/6-31G(d):LSDA/LANL2MB) model chemistry is available the wavenumbers are given unscaled. As expected, the deviation between the experimental and computed frequencies was quite similar to that for the B3LYP/6-31G(d) method [33].



Fig. 7. Free energy profile of the isomerization of Co₂(CO)₆(dppm).



Fig. 8. Free energy profile of the isomerization reactions of Co₂(CO)₅(dppm).

Table 3 Selected harmonic vibrational frequencies for complexes and transition states of $Co_2(CO)_n(dppm)$ type (n = 5, 6)

| Structure | $v (cm^{-1})$ |
|--------------|---|
| 1 | 1840, 1943, 2080, 2087, 2106, 2137 |
| 1TS | 21i, 2000, 2021, 2062, 2076, 2094, 2132 |
| 1a | 2005, 2028, 2062, 2073, 2093, 2132 |
| 3a | 1869, 1923, 2079, 2083, 2122 |
| 3aaTS | 34i, 1924, 2030, 2048, 2081, 2114 |
| 3abTS | 103i, 1875, 2008, 2064, 2083, 2117 |
| 3b | 1923, 2040, 2075, 2082, 2130 |

3.7. CO dissociation in $Co_2(CO)_5(CHCO_2Et)(dppm)$ complexes

As possible isomers of $Co_2(CO)_5(CHCO_2Et)(dppm)$, four complexes have been considered. Two with the bridging ethoxycarbonylcarbene group in *cis*-position to dppm and two with *trans*-position, both with two possible orientations of the ethoxycarbonyl group, as depicted in Fig. 9. The free energy of the CO dissociation of **2** is 30.1 kcal/ mol, significantly higher than that of **1**. However, the rate of the ¹³CO exchange is more than twice for **2** compared to 1, thus the CO dissociation of 2 resulting in 4 is not expected to be involved in the preferred pathway for CO exchange. Complex 2a is very close to 2 in energy, however, the free energy of dissociation is 24.0 kcal/mol, still higher than an expected value being in accordance with the higher rate of the CO exchange of 2. The CO dissociation in complex 2b is smaller than in any of the four isomers (7.5 kcal/ mol), however, the reaction takes place via a transition state; the free energy barrier is 20.8 kcal/mol. Complex 2c, which is higher in free energy by 5.6 kcal/mol and may be originated from 2 by an arm-off dissociation of the phosphane ligand followed by an isomerization, contains a loosely bound terminal carbonyl ligand with a significantly lower free energy of dissociation (12.2 kcal/mol) compared to 2 and 2a. Thus, this pathway is predicted to be the possible route in the ¹³CO exchange reaction of complex 2. The harmonic vibrational data of complexes containing ethoxycarbonyl carbene ligand are given in Table 4.

4. Conclusions

In this paper the structures of $Co_2(CO)_6(dppm)$ (1) and $Co_2(CO)_5(CHCO_2Et)(dppm)$ (2) and the rate of their



Fig. 9. Geometries and Gibbs free energies of CO dissociation of isomers of Co₂(CO)₅(CHCO₂Et)(dppm). Free energy values are given in kcal/mol.

Table 4 Selected harmonic vibrational frequencies for complexes of $Co_2(CO)_n(CH-CO_2Et)(dppm)$ type (n = 4, 5)

| Structure | $v (cm^{-1})$ |
|-----------|------------------------------|
| 2 | 1803, 1953, 2095, 2114, 2141 |
| 2a | 1932, 2089, 2108, 2137 |
| 2b | 1840, 2083, 2093, 2109, 2134 |
| 2c | 1860, 2089, 2108, 2131 |
| 4 | 1915, 2077, 2088, 2118 |
| 4a | 1906, 2074, 2076, 2116 |
| 4b | 1849, 2071, 2082, 2110 |
| 4c | 1911, 2077, 2081, 2126 |

reaction with external carbon monoxide has been discussed. The structures of both complexes show asymmetry with respect to the orientation of the phenyl groups. The effect of this asymmetry was recognized in the solid-state ³¹P NMR spectra of **1** and **2** and in the solid-state and solution ¹³C NMR spectra of **2** as well, but not in the solid-state and solution ¹³C NMR spectra of **1**. The crystal structure of 2 revealed that the ethoxycarbonylcarbene group replaces one of the bridging carbonyls in complex 1. which was closer to the phosphorus atoms. According to the computational results the structure with this position and orientation of the ethoxycarbonylcarbene group proved to be the lowest energy structure among the possible Co₂(CO)₅(CHCO₂Et)(dppm) isomers. In CH₂Cl₂ solution under an atmosphere of 13 CO, the CO ligands of both complexes exchange with ¹³CO. The overall rate of ¹³CO exchange at 10 °C was found to be 2.27 times higher for 2 than for 1. According to ONIOM studies the dominant pathway of CO dissociation of complex 2 is originated from the slightly higher energy isomer 2c bearing the ethoxycarbonylcarbene group trans to the dppm ligand. The solution NMR spectra of 1 indicate a fast exchange between the axial and equatorial and bridging and terminal positions of the carbonyl groups, respectively. Accordingly, the free energy barrier of the interconversion of 1 into the semi-bridged structure **1a** is 6.1 kcal/mol.

5. Supplementary material

CCDC 648429 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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