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CHROMIUM, MOLYBDENUM AND TUNGSTEN CARBONYL DERIVATIVES OF AN UNUSUAL OXYGEN TRIPOD LIGAND

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Summary

(Cyclopentadienyl)tris(diethylphosphito-*P*)cobaltate(1–), $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$, reacts as an oxygen tripod ligand L^- with $(CH_3CN)_3M(CO)_3$ (M = Cr, Mo, W) in water to produce the tricarbonyl complexes $[LM(CO)_3]^-$. These anions react with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to give the nitrosyl compounds $[LM(CO)_2(NO)]$, (M = Cr, Mo or W). Further substitution with triethylphosphine yields $[LMo(CO)(NO)(PEt_3)]$. The air-stable and volatile hydride complex $[LMo(CO)_3H]$ can be precipitated from an aqueous solution of $Na[LMo(CO)_3]$ by addition of acetic acid. Heating the molybdenum hydride $[LMo(CO)_3H]$ to 150°C in vacuo results in the formation of the metal–metal bonded species $[\{LMo(CO)_3\}_2]$; this compound, containing formal seven-coordinate molybdenum(I), is rigid on the NMR time scale at room temperature.

Introduction

We recently prepared a new type of oxygen tripod ligand $L^- = [(C_5R'_5)M\{P(O)R_2\}_3]^-$, where R′ = H, CH_3, M = Co, Rh; R = alkyl, *O*-alkyl [1]. The ligand field spectra of the transition metal complexes ML_2 (M = Co, Ni or Cu) characterize these ligands as unexpectedly hard and very weak ligands, similar to water and fluoride [2]. Since oxygen ligands and other strongly electronegative ligands such as fluoride normally form only labile and thermally unstable Group VI metal carbonyl derivatives [3], we were surprised to find that the oxygen tripod ligand $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$ forms very stable metal carbonyl hydride and nitrosyl complexes. We describe below the synthesis and spectroscopic characterization of these compounds.

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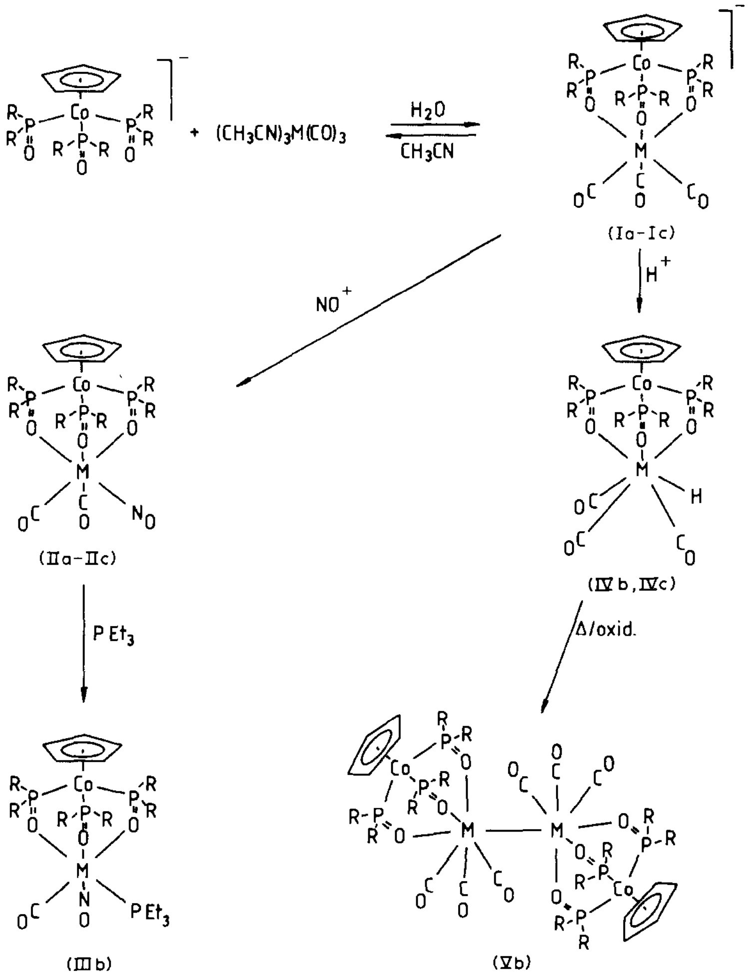

SCHEME 1. M = Cr (a); M = Mo (b); M = W (c).

Results and discussion

The tripod ligand $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$ (hereafter abbreviated as L^-) in the form of its sodium salt reacts readily with $(CH_3CN)_3M(CO)_3$ (M = Cr, Mo, W) in water and many organic solvents to give dark red solutions of $Na[LM(CO)_3]$. Such solutions are sensitive to air oxidation but hydrolytically stable at room temperature under an inert atmosphere. The tetraphenylphosphonium salts $PPh_4[LMo(CO)_3]$ can be precipitated from aqueous solutions by adding tetraphenylphosphonium bromide. After recrystallization from acetone or methylene chloride the salts show molar conductivities in nitromethane typical of 1 : 1 electrolytes with large anions [4]. When we prepared the anion Ib directly from an equimolar mixture of 0.1 mmol NaL and $Mo(CO)_6$ in 10 ml acetonitrile, roughly equal amounts of $(CH_3CN)_3Mo(CO)_3$ and $[LMo(CO)_3]^-$ were obtained after heating under reflux for

2 h. The same equilibrium is reached rapidly at room temperature, as judged from the IR spectra, when Na[LMo(CO)$_3$] is dissolved in acetonitrile. Acetonitrile can evidently compete with L$^-$ in this ligand displacement reaction.

The reaction with triethylphosphine does not bring about displacement of carbon monoxide, but rather replacement of the L$^-$. Replacement of a CO ligand in Ia, Ib and Ic is, however, possible with NO$^+$. We used *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide as the nitrosylation agent for the preparation of [LM(CO)$_2$(NO)] (IIa, IIb, IIc, see Experimental section). Complexes IIb and IIc are air-stable whereas IIa slowly decomposes in air. The substitution of one CO ligand by NO$^+$ reduces the local C_{3v} symmetry at M in I to C_s in II, as shown in Fig. 1.

The six OC$_2$H$_5$ substituents which are isochronous in I are therefore expected to give rise to three different groups of signals in the ^{1}H NMR spectra of II. The signal of the methylene protons is too complex for analysis but the anisochrony of the methyl groups is evident from the 60 MHz ^{1}H NMR spectra. The IR spectra show the typical pattern of the ligand L$^-$ [5], two strong and sharp ν(CO) bands, and the NO stretching vibration, consistent with the proposed structure of II.

The nitrosyl complex IIb reacts with triethylphosphine to give the CO replacement product IIIb. This is in contrast to the reaction of Ib with PEt$_3$ which, as mentioned above, leads to displacement of the L$^-$. The different behaviour of Ib and IIb clearly reflects the balance of labilization and stabilization of the metal–carbon monoxide bonds. It is seen from the CO stretching frequencies that the π-acceptor ability of NO$^+$ effectively compensates for the stabilization by the donor property of the oxygen donor L$^-$.

The anions [LMo(CO)$_3$]$^-$ (Ib) and [LW(CO)$_3$]$^-$ (Ic) react with acetic acid to give the neutral hydrides [LM(CO)$_3$H] (IVb, IVc). The expected protonation of the oxygen ligand and subsequent elimination of HL and formation of the acetate complexes M$_2$ac$_4$ do not occur. Instead the protonation results in the formation of a molybdenum–hydrogen or tungsten–hydrogen bond as evidenced by the ^{1}H NMR spectra of IVb and IVc. The hydride signals of IVb and IVc appear at -4.1 and -2.9 ppm in methylene chloride-d_2. In acetone-d_6 there is rapid exchange of the molybdenum hydride with deuterium from the solvent. The tungsten hydride complex is inert towards H/D exchange under these conditions at least during several hours. Both compounds can be handled in air. They are thermally very stable but are slightly sensitive to light. IVb has been sublimed at 100–120°C in high vacuum. The synthesis of IVb and IVc on a preparative scale is best accomplished by precipitating IVb and IVc from aqueous solutions of Na[LM(CO)$_3$] with acetic acid. To our

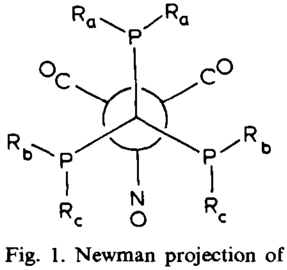

Fig. 1. Newman projection of II along the Co–M axis. The three types of anisochronous substituents R = OC$_2$H$_5$ are labelled a, b, c.

knowledge these are the first mononuclear molybdenum and tungsten carbonyl hydride complexes containing oxygen ligands [6].

Heating of the molybdenum hydride IVb to 140–200°C in vacuo for several hours leads to the formation of the dimeric viz. tetranuclear compound $[\{LMo(CO)_3\}_2]$ (Vb). This compound can also be prepared by slow air oxidation of the anion Ib, albeit in low yield. The dimeric nature of Vb is indicated by its mass spectrum showing M^+ and $M^+ - n$CO ($n = 1$–6) with $M^+ - 6$CO as the most intense peak. As judged from the IR spectrum Vb contains no carbonyl ligands in bridging positions. The pattern of the carbonyl region in the IR spectrum of Vb is similar to that of $[\{(C_5H_5)Mo(CO)_3\}_2]$ [9], which has led us to propose the structure of Vb as shown in the reaction scheme (Scheme 1).

The transoid arrangement of the oxygen ligands L^- is very probable for steric reasons on the basis of the molecular dimensions of L^- [10] and a Mo–Mo single bond length as found in $[\{(C_5H_5)Mo(CO)_3\}_2]$ [11]. The obvious question arises whether rotation of the oxygen tripod ligand L^- about its C_3 axis is a low energy process, i.e. whether Vb, containing formal seven-coordinate molybdenum(I), is a fluxional molecule. Such a rapid rotation of L would lead to isochrony of all the R groups. If the molecules were rigid on the NMR time scale and retained a plane of symmetry through the four metal centres, the 12 substituents R would give three different groups of NMR signals. The same symmetry arguments also predict two different ^{31}P NMR signals in the ratio 1/2 for a rigid structure of Vb. No

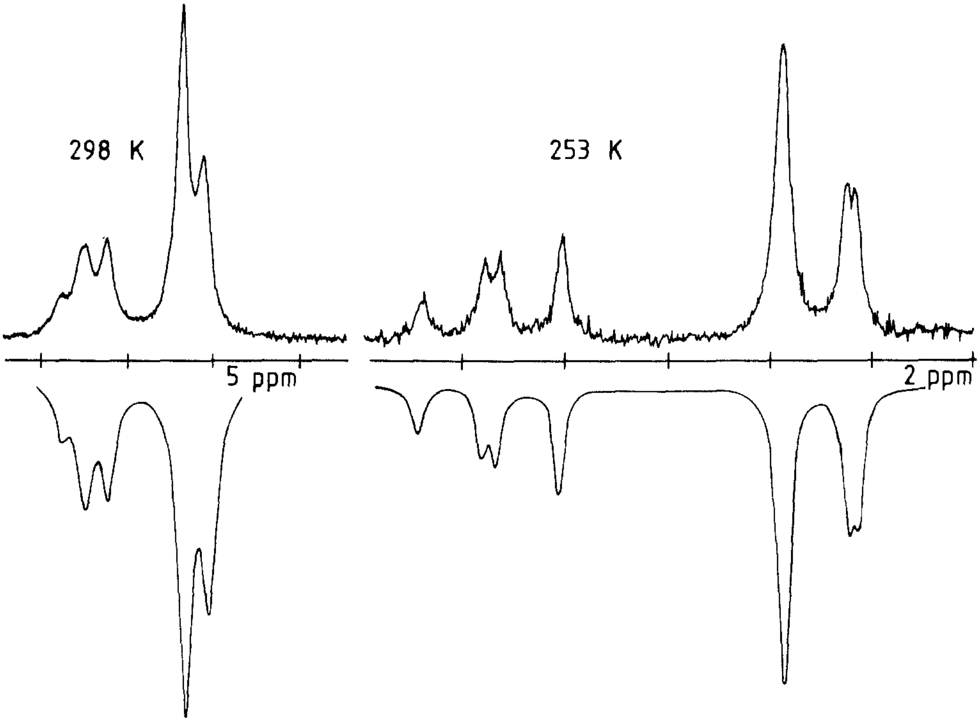

Fig. 2. 109 MHz $\{^1H\}$ ^{31}P NMR spectra of Vb measured at 298 and 253 K (top) and calculated (bottom) using the parameters given in the experimental part. Half width ca. 100 Hz at 298 K, ca. 27 Hz at 253 K.

anisochrony of the groups R was detectable in the 60 MHz ^{1}H NMR spectrum of Vb at room temperature, but an AB_2 pattern was observed in the ^{31} P NMR spectrum. In Fig. 2 are shown the $\{^{1}H\}$ ^{31}P NMR spectra measured at +25 and −20°C at 109 MHz (top) and (bottom) simulated by use of the least squares parameters given in the Experimental part.

The appearance of the room temperature spectrum is strikingly different from that at low temperature. The former is not, however, an AB_2 spectrum starting collapse because of rotation of the oxygen tripod ligand nor is it due to different populations of rotamers of Vb. It is, in fact, merely a consequence of the difference in line widths of the ^{31}P signals, as is clearly demonstrated by the simulated spectra. The different line widths are due to the temperature dependence of the quadrupole relaxation of the ^{59}Co nucleus. The same kind of line broadening has been observed in the ^{31}P NMR spectra of NaL and other metal complexes of L^-. We are currently investigating whether the seven-coordinate molybdenum centres in Vb are also stereochemically rigid at higher temperatures.

Concluding remarks

The metal carbonyl complexes containing the weak and hard oxygen ligand L^- are surprisingly stable, and we cannot offer a completely satisfactory explanation of why this should be so. Much of the stability of the M–L bond could be due to the chelate effect of the tridentate ligand. We have found that the equilibrium constants for the complex formation reactions

$$L^- + M^{n+}_{aq} \rightleftarrows ML^{(n-1)+}_{aq}$$

are very high indeed. Furthermore the formation of the complex is completely dominated by the entropy term [12]. The ligand L^- seems to have an ideal geometry for the formation of facial metal complexes without loss of much internal rotational entropy upon coordination.

The very low CO stretching frequencies of I and the compounds derived from it contrast with the early position of L^- in the spectrochemical series [2]. We postulate that L^- is a weak ligand not so much because it is a weak σ donor but because it is a fairly strong π donor [13]. Qualitative MO considerations show that good π donation by the ligands makes the ligand field splitting Δ_0 smaller by increasing the energy of the t_{2g} derived orbitals [16]. This in turn lowers the energy separation between these d orbitals and the CO π^* orbitals, causing better M–CO back donation and lower $\nu(CO)$ values. A combination of very strong metal carbonyl bonds and the chelate effect of the oxygen tripod ligand L^- is therefore at least a plausible explanation for the observed high stability of the carbonyl complexes described in this paper. Preliminary experiments have shown that these compounds possess a rich chemistry, which will be described in a subsequent paper.

Experimental

The complexes $(CH_3CN)_3M(CO)_3$ (M = Cr, Mo, W) [17], $(DMF)_3W(CO)_3$ [18] and $Na[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3] \equiv NaL$ [19] were prepared by published procedures. All preparations were carried out under an inert atmosphere and all solvents were degassed before use unless otherwise stated. Infrared spectra were recorded on a Perkin–Elmer Model 283 and 580 spectrophotometer. 60 MHz ^{1}H NMR spectra were obtained on a Varian EM 360 instrument; ^{31}P Fourier-transform NMR spectra were determined at 109.3 MHz on a Bruker WH 270 instrument. The ^{31}P NMR spectra were analyzed and computer-simulated spectra were obtained using a modified version of the LAOCOON 3 program. Conductivity measurements were carried out on a Schott Model CG 851 conductivity bridge using a Schott LF 1050 dipping cell. Elemental analyses were by Analytische Laboratorien, H. Malissa und G. Reuter, Elbach/Engelskirchen.

$Na[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3Mo(CO)_3]$ (Ib, sodium salt)

A mixture of 280 mg (1.05 mmol) $Mo(CO)_6$ and 535 mg (1.05 mmol) NaL in 10 ml acetonitrile was heated under reflux for 3 h. The solvent was distilled off under reduced pressure and replaced by methylene chloride. After filtration and evaporation of the solvent the product was crystallized from methylene chloride/pentane. Yield 457 mg (59%) ochre yellow needles. ^{1}H NMR (CD_3COCD_3): δ(ppm) 1.2 (t, ^3J(HCCH) 7 Hz, 18H, CH_3); 4.0 (m, 12H, OCH_2); 4.7 (s, 5H, C_5H_5). IR (CH_2Cl_2, ν(CO)): 1880st; 1738st, br; 1710st, br cm^{-1}.

$PPh_4[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3M(CO)_3]$ (M = Cr, Mo, W) (Ia, Ib, Ic, tetraphenylphosphonium salts)

A solution of 520 mg (1.96 mmol) $Mo(CO)_6$ in 30 ml acetonitrile was heated under reflux for 16 h. The solvent was evaporated and the solid residue and 1.00 g (1.96 mmol) NaL were stirred overnight in 20 ml H_2O. The dark red solution was filtered and 820 mg (1.96 mmol) PPh_4Br was added to give a voluminous precipitate. This was dried, and recrystallized from acetone to give 1.10 g (53%) of reddish brown microcrystals. The chromium compound was prepared similarly in 76% yield based on pure $(CH_3CN)_3$ $Cr(CO)_3$.

The complex $(DMF)_3W(CO)_3$ could be used instead of $(CH_3CN)_3W(CO)_3$ as starting material for the tungsten compound. The mixture of $(DMF)_3W(CO)_3$ and NaL in water was kept at 80°C for 2 h before addition of PPh_4Br. Yield 55%.

All the compounds must be stored under an inert atmosphere. The molybdenum and the tungsten complex can, however, be handled in air for short periods of time without appreciable degradation. $PPh_4[LM(CO)_3]$ (M = Cr, Mo, W) ^{1}H NMR (CD_3COCD_3); δ(ppm) 1.2 (t, ^3J(HCCH) 7 Hz, 18H, CH_3); 4.0 (m, 12H, OCH_2); 4.7 (s, 5H, C_5H_5); 7.6–7.8 (m, 20H, C_6H_5). IR (CH_2Cl_2, ν(CO)): 1890st, 1734st (M = Cr): 1886st, 1729st (M = Mo); 1873st, 1720st cm^{-1} (M = W). Molar conductivity, M = Mo, c 7.5×10^{-4} mol l^{-1}: Λ 59 ohm^{-1} cm^2 mol^{-1}; M = W, c 1.2×10^{-3} mol l^{-1}: Λ 62 ohm^{-1} cm^2 mol^{-1}.

$[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3M(CO)_2(NO)]$ (M = Cr, Mo, W) (IIa, IIb, IIc)

To a dark red solution of 3.00 g (4.06 mmol) of the sodium salt of Ib in 20 ml water and 10 ml tetrahydrofuran were added 870 mg (4.06 mmol) *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide. After 4 h the colour of the solution had changed to yellow and an air-stable red oil had formed. The solution was concentrated under reduced pressure to ca. 10 ml and set aside overnight. The red oil was separated and dried in vacuo. It was crystallized from ethanol to give bright orange crystals. These were collected, washed with pentane and dried in vacuo to give 1.45 g (49%) IIb, m.p. 158–159°C. The compound is stable in air and can be sublimed at 140°C in high vacuum. Found: C, 31.62; H, 4.92; Mo, 13.51; P, 12.83. $C_{19}H_{35}CoMoNO_{12}P_3$ calcd: C, 31.82; H, 4.92; Mo, 13.38; P, 12.95%. The chromium and the tungsten compounds IIa, IIc were prepared similarly. Purification was by column chromatography on alumina with methylene chloride/pentane. The chromium compound IIa decomposes in air whereas IIc is air-stable. IIa, IIb, IIc have identical ^1H NMR spectra (CD_3COCD_3): δ(ppm) 1.3 (three t, separated from each other by ca. 0.02 ppm, ^3J(HCCH) 7 Hz, 18 H, CH_3); 4.1 (m, 12H, OCH_2); 5.0 (s, 5H, C_5H_5). IR (IIa, hexane, ν(CO), ν(NO)): 2025st, 1935sst, 1696st; (IIb, hexane, ν(CO), ν(NO)): 2004st, 1908sst, 1661st; (IIc, pentane, ν(CO), ν(NO)): 1994st, 1888sst, 1647st cm^{-1}.

$[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3Mo(CO)(NO)P(C_2H_5)_3]$ (IIIb)

A solution of 80 mg (0.11 mmol) IIb and 15 mg (0.13 mmol) triethylphosphine in 5 ml acetone was heated under reflux for 2 h. The solvent was removed under reduced pressure and the oily residue dried in high vacuum. Recrystallization from ether gave air-stable dark red crystals, which were washed with pentane and dried in vacuo, yield 59 mg (64%). ^1H NMR (CD_3COCD_3): δ (ppm) 0.8–1.9 (m, 33H, $P(C_2H_5)_3$ and CH_3); 4.2 (m, 12H, OCH_2); 5.0 (s, 5H, C_5H_5). IR (KBr, ν(CO), ν(NO)): 1860st, 1573st cm^{-1}.

$[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3Mo(CO)_3H]$ (IVb)

A solution of $Na[LMo(CO)_3]$ (Ib, sodium salt) was prepared from 535 mg (1.05 mmol) NaL and 280 mg (1.05 mmol) $Mo(CO)_6$ in boiling acetonitrile as described above. The solvent was slowly removed under reduced pressure and replaced by 20 ml water. After heating to 40–50°C for 30 min the solution was filtered at room temperature. Addition of 0.25 ml (4.4 mmol) acetic acid to the red solution precipitated the yellow hydride complex IVb. The precipitate was collected, washed with water, and dried in vacuo, yield 662 mg (88%). Complex IVb is sensitive to light but it can be exposed to air for some days without noticeable decomposition. It sublimes at ca. 100°C in high vacuum. Found: C, 33.20; H, 4.97; Mo, 13.25. $C_{20}H_{36}CoMoO_{12}P_3$ calcd.: C, 33.54; H, 5.07; Mo, 13.39%. ^1H NMR (CD_2Cl_2): δ(ppm) −4.1 (s, 1H, Mo–H); 1.3 (t, ^3J(HCCH) 7 Hz, 18H, CH_3); 4.1 (m, 12H, OCH_2); 4.9 (s, 5H, C_5H_5). IR (KBr): 1998st, 1890sst, 1870sst cm^{-1}.

$[\{(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3Mo(CO)_3\}_2]$ (Vb)

A solution of Ib, sodium salt, in acetonitrile was prepared from 500 mg (1.05 mmol) NaL and 280 mg (1.05 mmol) $Mo(CO)_6$ as described above and the acetonitrile was subsequently replaced by tetrahydrofuran. After heating the solution to 40°C for 15 min, 0.25 ml (4.4 mmol) acetic acid was added. The solvent was removed under reduced pressure and the solid residue was heated to 150°C for 4 h in vacuo then dissolved in methylene chloride. The solution was washed several times with water, then methanol was added and the solution was exposed to air. Large brown needles separated slowly. These were collected, washed with water and dried in vacuo, yield 323 mg (43%). Found: C, 33.46; H, 4.95; Mo, 13.55; P, 12.81. $C_{40}H_{70}Co_2Mo_2O_{24}P_6$ calcd: C, 33.58; H, 4.93; Mo, 13.41; P, 12.99%. ^1H NMR ($CDCl_3$): δ (ppm) 1.3 (t, ^3J(HCCH) 7 Hz, 36H, CH_3); 4.1 (m, br, 24H, OCH_2); 4.9 (s, 5H, C_5H_5). $\{^1H\}$ ^{31}P NMR ($CDCl_3$): AB_2 spectrum, δ(A) 118.24, δ(B) 112.15 ppm (rel. ext. H_3PO_4), ^2J(AB) 149 Hz. IR (KBr, ν(CO)): 1950m, 1880st, 1827st cm^{-1}.

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