ORGANOMETALLICS

Volume 9, Number 8, August 1990

## Communications

# Haloalkyl Complexes of Transition Metals: Preparation and Characterization of (Dichloromethyl)cobalt(III) Derivatives

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*Received March 5, 1990*

*Summary:* Dichloromethyl complexes of the type $[Co(CHCl_2)(CNR)_nP_{5-n}](PF_6)_2$ [$n$ = 2, 3; R = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-$ClC_6H_4$; P = $PhP(OEt)_2$] were prepared by allowing the compounds $[Co(CNR)_nP_{5-n}]PF_6$ to react at −80 °C with aryldiazonium cations in $CH_2Cl_2$. Their characterization by infrared and $^1H$, $^{13}C\{^1H\}$, and variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy is reported. Some studies on reactions with electrophiles and nucleophiles are also described.

Current interest in the chemistry of halomethyl complexes[1] is due to their potential use as precursors for important classes of compounds, including those with a terminal carbene ligand and bridging methylene or polymethylene groups. Oxidative addition reactions of dihalomethane to low-valent transition-metal complexes have been used as a useful method for the synthesis of these complexes.[1,2] In this way a number of derivatives containing the $MCH_2X$ group have been reported. In contrast, dihalomethyl $MCHX_2$ complexes are very rare.[3] We report here the first example, to our knowledge, of a new reaction that affords the synthesis of new cobalt(III) complexes containing a dichloromethyl ($CHCl_2$) group as ligand.

Cobalt(I) derivatives[4] $[Co(CNR)_2P_3]^+$ and $[Co(CNR)_3P_2]^+$ [R = 4-$CH_3C_6H_4$, a; 4-$CH_3OC_6H_4$, b; 4-$ClC_6H_4$, c; P = $PhP(OEt)_2$] react at room temperature with stoichiometric or excess amounts of aryldiazonium cations in $CH_2Cl_2$ to give dichloromethyl $[Co(CHCl_2)(CNR)_2P_3]^{2+}$ (1) and $[Co(CHCl_2)(CNR)_3P_2]^{2+}$ (2) complexes, respectively, in almost quantitative yields (≥90%), and these can be isolated as $PF_6^-$ or $BPh_4^-$ salts.[5,6] Evolution of $N_2$ was detected[7] during the reaction course and analysis of the

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(1) (a) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Ramirez, J. A. *J. Chem. Soc., Chem. Commun.* **1989**, 304, and references therein. (b) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; McAlees, A. J.; Sneddon, D. W. *J. Chem. Soc., Dalton Trans.* **1989**, 761. (c) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543. (d) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630.

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(5) All preparative work was carried out under inert atmosphere using standard Schlenk techniques; solvents used were degasssed and purified by standard methods. In a typical preparation, 5 mmol of the cobalt(I) complex $[Co(CNR)_3P_2]^+$ or $[Co(CNR)_2P_3]^+$ was mixed with a slight excess (5.2 mmol) of an aryldiazonium salt [generally $(4\text{-}CH_3C_6H_4N_2)^+BF_4^-$, 1.07 g] and cooled to −80 °C. $CH_2Cl_2$ (20 mL) was cooled to the same temperature and added to the solid. The reaction mixture was slowly brought to room temperature and stirred for 2 h. After filtration, the resulting solution was evaporated to dryness under reduced pressure, giving a brown oil, which was triturated with ethanol (20 mL). The addition of $NaBPh_4$ or $NaPF_6$ to the resulting orange–yellow solution caused the separation of a yellow solid, which was recrystallized from $CH_2Cl_2$ (5 mL) and ethanol (20–30 mL); yield ≥90%. Satisfactory elemental analyses were obtained for all complexes. As an example: Anal. Calcd for $C_{47}H_{60}N_2Cl_2CoF_{12}O_6P_5$, **1a**: C, 44.74; H, 4.79; N, 2.22; Cl, 5.62. Found: C, 44.54; H, 4.87; N, 2.37; Cl, 5.90. Anal. Calcd for $C_{45}H_{52}N_3Cl_2CoF_{12}O_4P_4$, **2a**: C, 45.78; H, 4.44; N, 3.56; Cl, 6.00. Found: C, 45.95; H, 4.49; N, 3.46; Cl, 6.20.

(6) In dichloroethane ($ClCH_2CH_2Cl$) as solvent, the reaction proceeds as in $CH_2Cl_2$, and the IR spectra of the solution ($\nu$(CN) at 2200 $cm^{-1}$ starting from $[Co(CNR)_2P_3]^+$) seem to suggest, by analogy, formation of the $[Co(ClCHCH_2Cl)(CNR)_2P_3]^{2+}$ complex. However, attempts to isolate a solid product failed because an oily material was always obtained. Instead, with $CHCl_3$ and $CH_2Br_2$ as solvents, the reaction did not proceed, and the starting cobalt(I) compounds could be isolated after 3 h of reaction.

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solution at the end of the reaction showed that the hydrocarbon ArH is also formed[7] (in a 1:1 ratio) as a product. The following stoichiometry of the reaction can therefore be proposed:

$$[\mathrm{Co(CNR)}_n\mathrm{P}_{5-n}]^+ + \mathrm{ArN_2}^+ + \mathrm{CH_2Cl_2} \rightarrow [\mathrm{Co(CHCl_2)(CNR)}_n\mathrm{P}_{5-n}]^{2+} + \mathrm{ArH} + \mathrm{N_2} \quad (1)$$

$$n = 2, 3 \quad \mathrm{Ar} = \mathrm{C_6H_5} \text{ or } 4\text{-}\mathrm{CH_3C_6H_4}$$

We have previously observed[8] that aryldiazonium cations can oxidize cobalt(I) to cobalt(II) and that the corresponding reduction at the aryldiazonium group[8,9] leads to unstable intermediates that decompose via $N_2$ and the aryl radicals. On this basis, we tentatively propose the reaction path[10] (2)–(4) for the formation of dichloromethyl complexes, involving the Co(I) → Co(II) oxidation of the starting complexes[11] with the formation of the aryl radical.

$$[\mathrm{Co^I(CNR)}_n\mathrm{P}_{5-n}]^+ + \mathrm{ArN_2}^+ \rightarrow [\mathrm{Co^{II}(CNR)}_n\mathrm{P}_{5-n}]^{2+} + \mathrm{Ar}^\bullet + \mathrm{N_2} \quad (2)$$

$$\mathrm{Ar}^\bullet + \mathrm{CH_2Cl_2} \rightarrow \mathrm{ArH} + \mathrm{CHCl_2}^\bullet \quad (3)$$

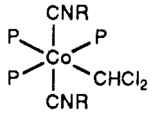
$$[\mathrm{Co^{II}(CNR)}_n\mathrm{P}_{5-n}]^{2+} + \mathrm{CHCl_2}^\bullet \rightarrow [\mathrm{Co^{III}(CHCl_2)(CNR)}_n\mathrm{P}_{5-n}]^{2+} \quad (4)$$

Presumably by abstraction of a hydrogen atom from $CH_2Cl_2$, Ar$^\bullet$ gives the observed hydrocarbon ArH and the new radical $CHCl_2^\bullet$, which, by reacting with the Co(II) complex, affords the final $[Co(CHCl_2)(CNR)_nP_{5-n}]^{2+}$ derivatives.

The new cobalt(III) complexes are pale-yellow solids, relatively stable as solids and in solution, diamagnetic, and 2:1 electrolytes[12] ($\Lambda_M$ for the $PF_6^-$ salts between 209 and 190 $\Omega^{-1}$ $M^{-1}$ $cm^2$ in $10^{-3}$ M solution of $CH_3NO_2$). Elemental analyses, including those of chlorine, infrared and $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopic data[13] support the proposed formulation.[14]

At room temperature, apart from phosphite and isocyanide signals, the $^1H$ NMR spectra show a triplet at $\delta$ 6.93 ($J_{PH_{app}}$ = 7.3 Hz) for compound $[Co(CHCl_2)(CNR)_3P_2]^{2+}$ (**2a**) and a quartet at $\delta$ 6.72 ($J_{PH_{app}}$ = 8.3 Hz) for related compound $[Co(CHCl_2)(CNR)_2P_3]^{2+}$ (**1a**), attributed to the Co–$CHCl_2$ group, the phosphite ligands being magnetically equivalent at this temperature. It may be noted that the previously reported monochloromethyl derivatives[1] show the $^1H$ signals of the M–$CH_2Cl$ fragment at $\delta$ 4.2–4.8, while in our case the appearance of these signals at a lower field ($\delta$ 6.7–6.9) supports the existence of the $CHCl_2$ ligand. In the $^{13}C\{^1H\}$ NMR spectra the dichloromethyl ligand signal appears as a quartet at $\delta$ 133.3 ($J_{CP}$ = 6 Hz) for **1a**, whereas a broad signal at $\delta$ 122.8 is observed for **2a**.

In the $\nu$(CN) region, the bis(isocyanide) $[Co(CHCl_2)(CNR)_2P_3]^{2+}$ (**1a**) complex shows only one strong band at 2197 $cm^{-1}$ ($CH_2Cl_2$), indicating two isocyanide ligands in a mutually trans position. The $^{31}P\{^1H\}$ NMR spectra in the temperature range +30 to −80 °C indicate that the complexes are fluxional. Moreover, also at −80 °C a broad multiplet is still present, and at lower temperatures the $A_2B$ multiplet expected for geometry I can probably be detected. On the other hand, no unambiguous assignment of a geometry in solution may be made for the $[Co(CHCl_2)(CNR)_3P_2]^{2+}$ (**2**) derivatives.



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The $^{31}P\{^1H\}$ NMR spectra appear as a sharp singlet at −80 °C, indicating the existence of two magnetically equivalent phosphorus atoms, but the IR spectrum shows only a rather large $\nu$(CN) band at 2206 $cm^{-1}$ ($CH_2Cl_2$), which does not allow us to distinguish between fac or mer geometry.

We studied the reactivity of the dichloroalkyl complexes toward electrophilic and nucleophilic reagents as well as reactions with $\pi$-acceptor ligands such as CO, CNR, phosphite, etc. Preliminary results show that no carbene complexes can be obtained by reaction of **1** or **2** with $Ag^+$, whereas reactions with acid such as $HBF_4$ do not proceed.

Treatment of both dichloroalkyl compounds **1** and **2** with $OH^-$, $Cl^-$, or $ArNH_2$ in any case affords the cobalt(I) tris(isocyanide) complex $[Co(CNR)_3P_2]^+$ as the final reaction product. In the case of reaction with $Cl^-$ the absence of chloroform ($CHCl_3$) was also observed in the solution, which could be formed by nucleophilic attack of $Cl^-$ on the carbon atom of the $CHCl_2$ ligand. Arylamine reacts with **1** or **2** and the infrared spectra taken during the reaction course do not display any intermediate containing isocyanide ligand beyond $[Co(CNR)_3P_2]^+$, as may be expected from the reaction of an amine on a chloroalkyl complex.[2e]

On the basis of these preliminary data, we can only conclude that, in the presence of $OH^-$, $Cl^-$, or $ArNH_2$, complexes **1** and **2** undergo a complicated reaction affording in any case the most stable complex in these conditions, the tris(isocyanide) $[Co(CNR)_3P_2]^+$ derivative.

Substitution of the ligands in $[Co(CHCl_2)(CNR)_nP_{5-n}]^{2+}$ is rather difficult, and no reaction was observed at room temperature with $\pi$-acceptor ligands such as CO (1 atm), CNR, and phosphite. In reflux conditions, however, re-

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(7) Dinitrogen was detected by gas chromatography, whereas the aromatic hydrocarbon ($C_6H_6$ or $CH_3C_6H_5$) was determined by both $^1H$ NMR and gas chromatography.

(8) Albertin, G.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1986**, 2551.

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(10) Studies of this reaction show that the time required for completion of reaction varies from about 10 to 100 min or more for a series of syntheses carried out under apparently identical conditions. Similarly, a variation in yield from 60 to 90% was also observed in some cases. This variability seems to suggest that a radical chain mechanism might be involved. To support this hypothesis, we attempted to trap intermediate alkyl or aryl radicals by using acrylonitrile as solvent since formation of such radicals should lead to polymerization of acrylonitrile. The reaction between Co(I) complexes and $ArN_2^+$ was therefore carried out using a mixture of $CH_2Cl_2$ and $CH_2$=CHCN (15:5 mL) as solvent. It was observed that, in this case too, the reaction gave the $[Co(CHCl_2)(CNR)_nP_{5-n}]^{2+}$ complexes. However, an insoluble product, characterized by infrared as poly(acrylonitrile), was also isolated from the reaction mixture, in agreement with the proposed radical pathway.

(11) It may be noted that when the progress of the reaction is monitored by IR spectra in the $\nu$(CN) region, besides the Co(I) and Co(III) absorptions, the presence of a small band at 2160 $cm^{-1}$ is revealed. This may be tentatively assigned to the $[Co^{II}(CNR)_nP_{5-n}]^{2+}$ intermediate. Instead, no direct information can be obtained from NMR spectra, because only very broad signals due to paramagnetic species occur during the reaction course.

(12) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(13) All NMR spectra were recorded in $(CD_3)_2CO$ with a Varian FT80-A instrument. $^1H$ and $^{13}C$ NMR chemical shifts are referred to internal $SiMe_4$; $^{31}P$ are referred to 85% $H_3PO_4$ with downfield shifts considered positive. $[Co(CHCl_2)(4\text{-}CH_3C_6H_4NC)_2\{PhP(OEt)_2\}_3](PF_6)_2$, **1a**: IR, $cm^{-1}$ ($CH_2Cl_2$) 2197 s, (KBr) 2196 s ($\nu$CN); $^1H$ NMR $\delta$ 7.86, 7.73, 7.48 (m, 23 H, Ph), 6.72 [q, ($J_{PH}$ = 8.3 Hz), 1 H, $CHCl_2$], 4.33 (m, 12 H, $CH_2$), 2.47 (s, 6 H, $CH_3$ isocy.), 1.49, 1.44 (t, 18 H, $CH_3$); $^{31}P\{^1H\}$ NMR $\delta$ (−80 °C) 142 (m, br); $^{13}C\{^1H\}$ NMR $\delta$ 133.3 [q, ($J_{CP}$ = 6 Hz), dichloroalkyl carbon]. $[Co(CHCl_2)(4\text{-}CH_3C_6H_4NC)_3\{PhP(OEt)_2\}_2](PF_6)_2$, **2a**: IR, $cm^{-1}$ ($CH_2Cl_2$) 2207 s (br) (KBr), 2206 s (br) $\nu$(CN); $^1H$ NMR $\delta$ 8.00, 7.63, 7.41 (m, 22 H, Ph), 6.93 [t, ($J_{PH}$ = 7.3 Hz), 1 H, $CHCl_2$], 4.60 (m, 8 H, $CH_2$), 2.46, 2.43 (s, 9 H, $CH_3$ isocy), 1.48 (t, 12 H, $CH_3$); $^{31}P\{^1H\}$ NMR, $\delta$ (−80 °C) 135.3 s; $^{13}C\{^1H\}$ NMR $\delta$ 122.8 (br, dichloroalkyl carbon).

(14) Attempts to obtain the X-ray crystal structure of compound **1a** failed because the crystal decomposes during the early stages of measurements. Pelizzi, G., private communication.

*Organometallics* **1990**, *9*, 2179–2181

duction to Co(I) was observed, always affording the $[Co(CNR)_3P_2]^+$ derivative.

**Acknowledgment.** The financial support of MPI and CNR, Rome, is gratefully acknowledged. Thanks are due to Daniela Baldan for her technical assistance.

**Registry No.** **1a**, 127518-91-6; **1b**, 127518-95-0; **1c**, 127518-97-2; **2a**, 127518-93-8; **2b**, 127518-99-4; **2c**, 127519-01-1; $[Co(CNR)_2P_3]PF_6$ (R = $4\text{-}CH_3C_6H_4$), 127518-87-0; $[Co(CNR)_3P_2]PF_6$ (R = $4\text{-}CH_3C_6H_4$), 127518-89-2; $(4\text{-}CH_3C_6H_4N_2)^+BF_4^-$, 459-44-9.

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# Aldehyde Insertion into a Platinum Hydride and Subsequent Nucleophilic Attack of the Alkoxide at Phosphorus: Platinum–Alkoxide/Phosphorus–Aryl Metathesis

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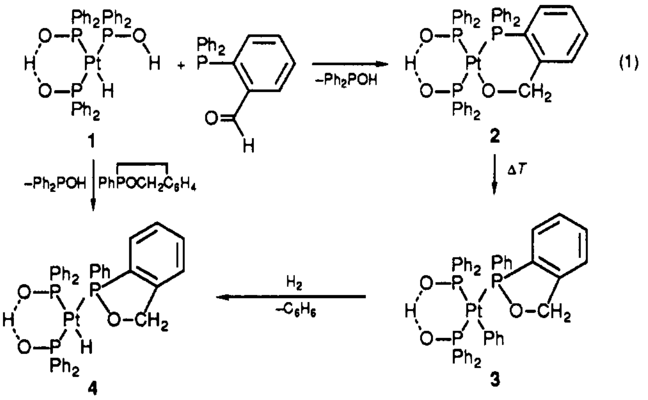
*Received February 22, 1990*

*Summary:* $Pt(Ph_2PO)(Ph_2POH)_2H$ (**1**) was treated with *o*-(diphenylphosphino)benzaldehyde to give a cyclic platinum alkoxide (**2**). The latter rearranges to the new product **3** (Scheme I), containing 1-phenyl-3*H*-2,1-benzoxaphosphole and a phenyl group coordinated to platinum, via a nucleophilic attack at the coordinated phosphorus center by the alkoxy group, followed by a shift of a phenyl group from phosphorus to platinum. The crystal structure of **3** has been determined.

The insertion of aldehydes into transition-metal hydrides plays a role in industrial processes such as the reduction of aldehydes to alcohols and the conversion of syngas to methanol or ethylene glycol.[1] In recent years the proposed intermediate alkoxide and hydroxymethyl late-transition-metal complexes have been prepared and their reactivity has been studied.[2–9] We have recently reported[10] on platinum phosphinito complexes that catalyze the hydroformylation of alkenes. The aldehydes are hydrogenated to alcohols in a secondary reaction, which may involve either alkoxy or hydroxymethyl intermediates. This communication deals with the mechanism of the aldehyde hydrogenation reaction in a model compound using *o*-(diphenylphosphino)benzaldehyde as the substrate. The resulting complex shows an unexpected rearrangement reaction that is related to the decomposition of arylphosphines in syngas reactions with late-transition-metal catalysts.

When $Pt(Ph_2PO)(Ph_2POH)_2H$ (1) was treated with *o*-(diphenylphosphino)benzaldehyde,[11,12a,b] one of the $Ph_2POH$ ligands was immediately replaced and the resulting product showed that insertion[12c] of the aldehyde into the platinum–hydride bond had occurred. $^1H$ and $^{31}P$ NMR spectroscopy revealed[13] that the platinum alkoxide 2 had been formed. Insertion of $Ph_2P(o\text{-}C_6H_4CHO)$ into a metal hydride may give either an alkoxy- or an ($\alpha$-hydroxyalkyl)metal complex. Thermodynamic studies[2,4,6] indicate that noncyclic alkyl- and alkoxyplatinum species have equal stabilities. In the present reaction both the five-membered ring (with an $\alpha$-hydroxyalkyl group) and the six-membered ring (with an alkoxy group) should be accessible since chelating phosphinoalkenes[14] react with platinum hydride 1 to give products with ring sizes ranging from three to seven. Molecular models show that the five-membered ring may be slightly more favorable. Also,

**Scheme I**



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(12) $o\text{-}Ph_2PC_6H_4CHO$ has been employed in reactions with Vaska's complex[12a] and $PtCl_2$[12b] to give oxidative addition of the aldehyde to the metal: (a) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506. (b) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045. Depending on the other ligands, the reactions involving aldehyde C–H bond breaking can be very facile, as is the case for quinoline-8-carbaldehyde,[12c] and for the present reaction more complicated mechanisms other than straightforward aldehyde insertion might be envisaged: (c) Anklin, C. G.; Pregosin, P. S. *J. Organomet. Chem.* **1983**, *243*, 101.

(13) $^{31}P$ NMR for **2** ($CD_2Cl_2$): $\delta(Ph_2PO)$ 72.0, $^1J(PtP) = 3100$ Hz, $^2J(PP\ trans) = 420$ Hz, $^2J(PP\ cis) = 30$ Hz; $\delta(Ph_2PC_6H_4CH_2O\text{–})$ 13.0, $^1J(PtP) = 2180$ Hz, $^2J(PP\ trans) = 420$ Hz, $^2J(PP\ cis) = 9.0$ Hz; $\delta(Ph_2POH)$ 61.0, $^1J(PtP) = 3420$ Hz, dd, cis couplings. $^1H$ NMR: $\delta$ 3.92 (2 H), $^3J(PH) = 9$ Hz, $^2J(PtH) = 33$ Hz; $\delta$ 6.4–8.0 (34 H).

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