*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

## PRELIMINARY COMMUNICATION

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# PHOSPHINE COBALT HYDRIDES AND PHOSPHINE NITROGEN COBALT HYDRIDE COMPLEXES VIA THE ALKYLALUMINIUM HYDRIDE ROUTE

J. LORBERTH, H. NÖTH and P.V. RINZE
*Institut für Anorganische Chemie der Philipps-Universität, Marburg (Deutschland)*
(Received November 4th, 1968)

Starting from simple cobalt(III) or cobalt(II) compounds, several preparations of $(Ph_3P)_3CoH_3$ and its reaction product with nitrogen, $(Ph_3P)_3CoHN_2$, have been reported, using $Et_2AlOEt$[1], iso-$Bu_3Al$ [2] or $NaBH_4$ [3,4] as reducing agents.

The conflicting reports on their stoichiometry now appear to be resolved[5], but spectroscopic data for the compounds, including their deuterated analogues, are so far poorly correlated. In order to study the effect of *para*-substitution of the arylphosphine ligands upon both the reactivity and thermodynamic stability of this type of compound we have prepared the complexes I–IV according to eqn. (1) (see Table 1). Di-n-butylaluminium hydride was used as a convenient reducing agent:

$$Co(acac)_n \xrightarrow[\text{n-}Bu_2AlH]{Et_2O/(p\text{-}RC_6H_4)_3P/Ar \text{ or } H_2} [(p\text{-}RC_6H_4)_3P]_3CoH_3 \qquad (1)$$

$(n = 2, 3)$

$$[(p\text{-}RC_6H_4)_3P]_3CoH_3 \xrightarrow[Et_2O/C_6H_6]{N_2} [(p\text{-}RC_6H_4)_3P]_3CoHN_2 + H_2 \qquad (2)$$

Reaction of these hydrides with molecular nitrogen according to eqn.(2) led to the corresponding nitrogen complexes V–VIII (see Table 1). Compounds I–IV contained one mole of solvent,*e.g.* $Et_2O$ or $C_6H_6$, and did not lose it on prolonged vacuum drying ($10^{-2}$ mm). This has been checked by analysis and $^1H$ NMR spectroscopy.

We failed to prepare crystalline compounds with ligands other than triarylphosphines; using the bidentate ligand $Ph_2PCH_2CH_2PPh_2$ (TPE) we obtained the well-known $(TPE)_2CoH$ in almost quantitative yield:

$$Co(acac)_3 \xrightarrow[\text{n-}Bu_2AlH]{Et_2O/TPE/H_2} (TPE)_2CoH \qquad (3)$$

Compounds V–VIII are solvate-free after vacuum drying for some hours, but they may be obtained as solvates when recrystallized at room temperature and dried only for a

TABLE 1

REACTION CONDITIONS FOR $[(p\text{-RC}_6\text{H}_4)_3\text{P}]_3\text{CoH}_3\cdot\text{Et}_2\text{O}$ AND $[(p\text{-RC}_6\text{H}_4)_3\text{P}]_3\text{CoHN}_2$ COMPLEXES[a]

| R | $\text{Co(acac)}_3$ (g) | Phosphine (g) | $\text{Et}_2\text{O}$ (ml) | $\text{n-Bu}_2\text{AlH}$ (ml) | Yield[b] (%) | Product | Co-hydride (g) | Yield (%) | Product |
|---|---|---|---|---|---|---|---|---|---|
| $\text{CH}_3$ | 2.70 | 6.9 | 100 | 4.5 | 47.5 | $[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_3\text{CoH}_3\cdot\text{Et}_2\text{O}$ (I) | 2.8 | 65 | $[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_3\text{CoHN}_2$ (V) |
| H | 2.70 | 6.0 | 150 | 4.0 | 60.0 | $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{CoH}_3\cdot\text{Et}_2\text{O}$ (II) | 4.2 | 97 | $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{CoHN}_2$[c] (VI) |
| F | 2.70 | 7.2 | 100 | 5.0 | 54.3 | $[(p\text{-FC}_6\text{H}_4)_3\text{P}]_3\text{CoH}_3\cdot\text{Et}_2\text{O}$ (III) | 1.2 | 78 | $[(p\text{-FC}_6\text{H}_4)_3\text{P}]_3\text{CoHN}_2$ (VII) |
| Cl | 3.85 | 13.2 | 150 | 10.0 | 68.0 | $[(p\text{-ClC}_6\text{H}_4)_3\text{P}]_3\text{CoH}_3\cdot\text{Et}_2\text{O}$ (IV) | 4.5 | 62 | $[(p\text{-ClC}_6\text{H}_4)_3\text{P}]_3\text{CoHN}_2$ (VIII) |

[a] Hydrides obtained in a hydrogen atmosphere, $\text{L}_3\text{CoHN}_2$ complexes prepared by bubbling nitrogen through a hydride solution for 25 min. [b] Yields based on cobalt starting material. [c] Prepared by the method of Misono *et al.* [2], precipitating VI with n-pentane.

TABLE 2

IR-FREQUENCIES OF COMPOUNDS I–VIII ($\text{cm}^{-1}$, IN NUJOL) AND $^1\text{H}$ NMR DATA, CHEMICAL SHIFTS $\delta$(Co-H) AND COUPLING CONSTANTS $J(^{31}\text{P}-^1\text{H})$ IN $\tau$

| Compound | $\nu(\text{N}_2)$ | Compound | $\nu_{as}(\text{CoH}_2)$ | $\nu_s(\text{CoH}_2)$ | $\nu(\text{CoH})$ | Compound | $\delta$(Co-H) | $J(^{31}\text{P}-^1\text{H})$ | Solvent | Internal standard |
|---|---|---|---|---|---|---|---|---|---|---|
| V | 2079 (2074, 2089)[a] | I | 1767 | 1895 | 1934 | II | 21.55 | 0.32 | $\text{C}_6\text{D}_6$ | TMS |
| VI | 2090 (2082, 2094 (sh))[a] | II | 1754 | 1887 | 1939 | II | 20.96 | 0.36 | THF | THF |
| VII | 2085 | III | 1767 | 1895 | 1946 | III | 21.75 | 0.32 | THF | THF |
| VIII | 2067 (2103)[b] | IV | 1801 | 1908 | 1955 | IV | 21.84 | 0.28 | THF | THF |

[a] Precipitated from $\text{C}_6\text{H}_6/\text{Et}_2\text{O}$ at -20°. [b] KBr pressed disc.

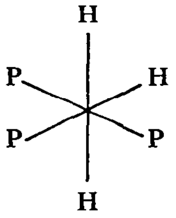
short period. Hydrolysis of I—VIII led to the elimination of $H_2$ or $H_2$ and $N_2$ following (4) or (5):

$$[(p\text{-}RC_6H_4)_3P]_3CoH_3 \xrightarrow[HCl]{H_2O/CH_3OH} [(p\text{-}RC_6H_4)_3P]_3CoCl + 2H_2 \qquad (4)$$

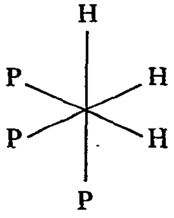
$$[(p\text{-}RC_6H_4)_3P]_3CoHN_2 \xrightarrow[HCl]{H_2O/CH_3OH} [(p\text{-}RC_6H_4)_3P]_3CoCl + H_2 + N_2 \qquad (5)$$

The ratio of 2 moles $H_2$ per mole of complex and the formation of tris(triarylphosphine)-cobalt(I) chloride from compounds I–IV strongly supports their formulation as trihydrides.

Table 2 lists the IR- and $^1$H NMR data obtained with a Perkin–Elmer 225 and a Varian HA 100 spectrometer. For *trans*-$L_3CoH_3$ complexes of $C_{2v}$-symmetry (A) three IR-active fundamental vibrations for the Co—H linkages are to be expected: $\nu_{as}(CoH_2)$ $(B_2)$, $\nu_s(CoH_2)$ $(A_1)$ and $\nu(CoH)$ $(A_1)$ with relative intensities strong, weak and medium, while for a *cis*-$L_3CoH_3$ complex of $C_{3v}$-symmetry (B) only two absorptions are anticipated: $\nu_s(CoH_3)$ $(A_1)$ and $\nu_{as}(CoH_3)$ $(E)$.



(A)



(B)

Our results favour a *trans*-tris(triarylphosphine)cobalt trihydride complex; Sacco *et al.*[4] came to the same conclusion, argueing on the basis of only two observed Co—H stretching modes and neglecting a band at 1887 $cm^{-1}$ in their reproduced spectrum[4], attributable to $\nu_s(CoH_2)$.

Trends in $\nu(CoH)$ are rationalized by the strong influence of *para*-substituents of the arylphosphine ligand *trans* to the Co—H bond. Changes in $\nu(Co—H)$ follow qualitatively the expected order of increasing electron-withdrawing character of the substituents R in the sequence $CH_3 < H < F < Cl$

This *trans* model would further imply two magnetically non-equivalent types of hydrogen atoms, two *cis* to the phosphine ligands and the unique hydrogen atom *trans* to one phosphine ligand, but this has not been observed so far, and integration of the $^1$H NMR spectra of these diamagnetic compounds has proved to be difficult. IR-spectra of the $L_3CoHN_2$ complexes did not reveal a significant absorption assignable to $\nu(Co—H)$. This may be due to a more hydridic nature of the hydrogen atom in $L_3CoHN_2$ than in $L_3CoH_3$, shown by the $^1$H NMR spectra of II and VI, where $\delta(Co—H)$ shifts from about 20.5 $\tau$ for II to about 29 $\tau$ for VI [5].

The $\nu(N_2)$-stretching mode is remarkably dependent upon crystal and solvent effects; Influences of the substituents R seem to be of minor importance and therefore interpretation of changes in $\nu(N_2)$ must be postponed until more data are available.

## EXPERIMENTAL

*I.* 10 ml (8.1 g, 57 mmole) n-$Bu_2AlH$ were added slowly over a period of 20 min. to a chilled mixture (-20°) of 3.85 g (10.8 mmole) $Co(acac)_3$ and 13.2 g (36.1 mmole) of $(p\text{-}ClC_6H_4)_3P$ in 100 ml $Et_2O$, stirred in a three-necked flask fitted with hydrogen-inlet, dry-ice/methanol condenser and dropping funnel. The solution was warmed to room temperature and stirred for one hour. During this time hydrogen was bubbled through the reaction mixture; the resulting yellow precipitate was filtered under a hydrogen atmosphere, washed several times with 20 ml portions of deoxygenated $Et_2O$ and vacuum dried at $10^{-2}$ mm. Yield: 9.05 g (68%) $[(p\text{-}ClC_6H_4)_3P]_3CoH_3 \cdot Et_2O$.

*II.* 4.5 g (3.65 mmole) of this hydride were partially dissolved in 50 ml $Et_2O/C_6H_6$ (1/1) and nitrogen was bubbled through this mixture until the compound had completely reacted and the colour had turned to deep red-orange. After evaporation of the solvent, the remaining red paste was dissolved again in a minimum of $Et_2O$ at room temperature and the solution allowed to crystallize at -20°. Filtration and vacuum drying at $10^{-2}$ mm yielded 2.7 g (62%) $[(p\text{-}ClC_6H_4)_3P]_3CoHN_2$.

*III.* 27 ml (21.9 g, 154 mmole) n-$Bu_2AlH$ and a mixture of 24 g (60 mmole) TPE and 7.72 g (30 mmole) $Co(acac)_3$ in 250 ml $Et_2O$ were reacted in the same way as in prep. I; $(TPE)_2CoH$ was isolated under nitrogen atmosphere, yielding 22.5 g (87%).

## ACKNOWLEDGEMENT

We thank the Badische Anilin- und Sodafabrik A.G., Ludwigshafen, for generous support and Schering A.G., Werk Bergkamen, for gifts of organoaluminium compounds.

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