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Simple syntheses of $Co_2(CO)_8$ and $NaCo(CO)_4$ reagents by the reduction of $CoCl_2$ (or $CoBr_2$) under carbon monoxide at atmospheric pressure

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Abstract

The reduction of $CoCl_2$ by MgH_2 in tetrahydrofuran in the presence of carbon monoxide gives $Co_2(CO)_8$, which on treatment with an alkyne and norbornene gives the Pauson–Khand reaction. The reduction of $CoCl_2$ or $CoBr_2$ by sodium naphthalenide in THF in the presence of carbon monoxide gives $NaCo(CO)_4$, which has been used for cyclization of certain benzylic halides into the corresponding cyclic ketones.

Introduction

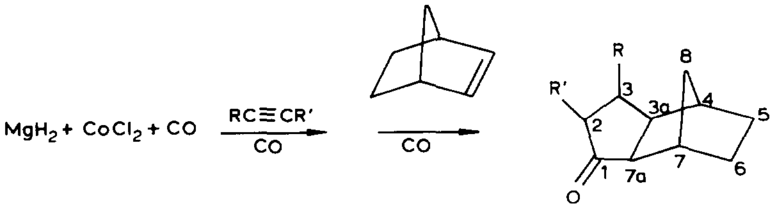
During our study of the development of simple routes for the synthesis of metal carbonyl reagents for use in organic synthesis [1a], it became of interest to prepare $NaCo(CO)_4$ reagent under non-aqueous conditions. The $NaCo(CO)_4$ reagent can be readily prepared by the reaction of NaOH with $Co_2(CO)_8$ under aqueous condition [2]. Sodium amalgum, Na–Hg [3], sodium potassium alloy, NaK [4], lithium trialkylborohydride, $LiBHEt_3$ [5], and potassium hydride, KH [6], have been used previously for the reduction of dicobaltooctacarbonyl to $NaCo(CO)_4$ under non-aqueous conditions. Although sodium amalgum was used successfully for the reduction of $Co_2(CO)_8$, it was later found out that it is the NaOH impurity present in Na–Hg which is responsible for this conversion. Though the use of sodium potassium alloy provides for a fast and clean reductive cleavage, more highly reduced species are also formed due to inadequate control of reaction time or temperature [4] and furthermore the use of Na–K always poses a potentially serious fire hazard. While the trialkylborohydride reagent is also effective for reductive cleavage of $Co_2(CO)_8$ into $Co(CO)_4^-$, it is necessary to remove the trialkylborane formed in the reaction. In view of the basic character of the carbonylate anion, there is a possibility of coordination of the trialkylborane to the anion, which might rule out its use for in situ generation of $NaCo(CO)_4$ for various organometallic syntheses. Though the reduction of dicobaltooctacarbonyl by KH does not give rise to the above problems, extreme care must be taken during the handling of the reagent. All of the above available procedures utilized the highly air sensitive $Co_2(CO)_8$ as starting material. We decided to explore the possibility of preparing the $NaCo(CO)_4$ reagent under non-aqueous condition by the direct reduction of CoX_2 using simple reducing reagents under atmospheric pressure at ambient temperature.

Results and discussion

We recently reported [1a] that the reduction of $CoCl_2$ by $NaBH_4$ in THF under carbon monoxide at 0 °C gives a species with strong metal carbonyl absorption at 1890 cm^{-1} characteristic of $Co(CO)_4^-$ species in THF solution [4]. However, the mixture prepared in this way also contains $>$B–H species which hydroborates alkenes [1b]. It was envisaged that the $Co(CO)_4^-$ reagent might be prepared by the reduction of $CoCl_2$ using a hydride free of boron species. We have found that NaH/THF is not effective for this purpose. The MgH_2 reagent [7], prepared in THF by the reaction of $MgBr_2$ and NaH on reaction with $CoCl_2$, under carbon monoxide at 0 °C gave a metal carbonyl reagent in solution, but it is not the expected $Co(CO)_4^-$ species, and the mixture failed to react with benzyl halides, a reaction characteristic of $Co(CO)_4^-$. However, the carbonyl reagent formed in this way does undergo the Pauson–Khand reaction with alkynes and norbornene [8], a transformation known with $Co_2(CO)_8$, as outlined in the Scheme 1. The yields are comparable with those obtained by following the previously described procedure [9].

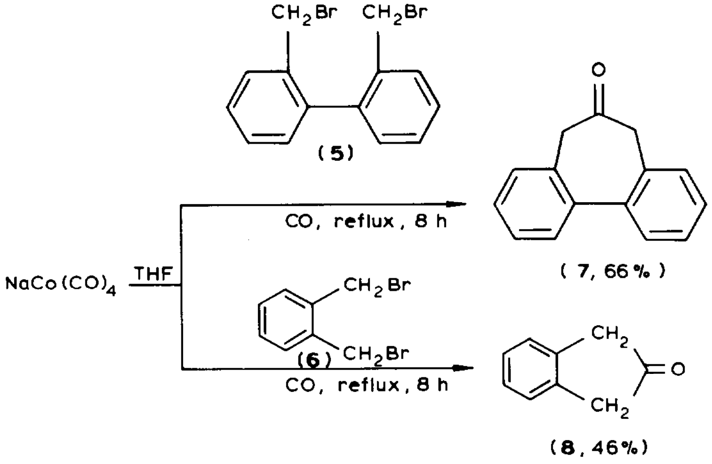
Comparison of the solution IR spectrum of authentic $Co_2(CO)_8$ in THF [10], also indicates that the species formed by the reduction of $CoCl_2$ by MgH_2 under carbon monoxide is $Co_2(CO)_8$ (IR absorptions at 2050, 1940, 1910 and 1820 cm^{-1}). Though $Co_2(CO)_8$ is known to disproportionate in THF within several days [6], we found no difficulty in utilizing the reaction mixture for the Pauson–Khand reaction. As the reduction of $CoCl_2$ with MgH_2 gives only $Co_2(CO)_8$, we were looking for some other simple reducing agent for the purpose.

Sodium naphthalenide has been utilized to reduce $Cr(CO)_6$ to the corresponding $Na_2Cr(CO)_5$ [11], and we expected that the reduction of $CoCl_2$ or $CoBr_2$ by sodium naphthalenide in THF under carbon monoxide atmosphere would give $NaCo(CO)_4$ in solution and this is indeed the case. We found that either $CoBr_2$ or $CoCl_2$ can be



	Yield (%)
R = H, R' = n – C_8H_{17} (1)	66
R = H; R' = Ph (2)	53
R = R' = n – C_3H_7 (3)	27
R = R' = Ph (4)	40

Scheme 1



Scheme 2

reduced to $Co(CO)_4^-$ under carbon monoxide with sodium naphthalenide as a reducing agent (naphthalene was used in a catalytic amount).

$$\begin{array}{ll} CoBr_2/CoCl_2 + Na/\text{naphthalene} & \xrightarrow[\text{3 h,RT}]{\text{THF,CO}} Na[Co(CO)_4] \\ \quad (10\ \text{mmol}) \qquad (30/10\ \text{mmol}) & \end{array}$$

The exclusive formation of $NaCo(CO)_4$ was shown by its characteristic very strong absorption at 1890 cm^{-1} in IR spectrum of the reaction mixture [4]. No other peak in the carbonyl region was observed, indicating the absence of any other cobalt carbonyl species. The reagent prepared in this way was used for carbonylative cyclization of certain benzyl halides (Scheme 2) [12].

The presence of naphthalene in the reaction medium did not give rise to any side product, and the naphthalene can be readily separated from the products. The new in situ syntheses of the metal carbonyl reagents using simple readily available chemicals under an atmospheric pressure of carbon monoxide would make synthetic methods involving these carbonyl derivatives more attractive, since in addition to making the metal carbonyl readily accessible for the synthetic applications, it also alleviates the problems involved in the storing and handling of metal carbonyl reagents.

Experimental

Melting points were determined on a Buchi-510 capillary point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer IR spectrometer Model-257 with polystyrene as reference. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer with chloroform-*d* as a solvent and TMS as reference ($\delta = 0$ ppm). Elemental analyses were performed on a Perkin-Elmer elemental analyser model 240C. Carbon monoxide was generated by adding HCOOH (98–100%) to concentrated H_2SO_4 following the procedure described for carbonylation of organoboranes [13].

General procedure for the preparation of MgH_2 slurry in THF [7]

The $MgBr_2$ (20 mmol) solution in THF (60 ml) was prepared by the reaction of Mg (20 mmol) with 1,2-dibromoethane (20 mmol) under nitrogen at room temperature during 3 h. NaH (30 mmol, dispersion in oil) was placed in a three-necked 250 ml RB flask under nitrogen by glove bag techniques. The oil was removed by washing with dry THF (2 × 15 ml) under nitrogen. The solution of $MgBr_2$ (20 mmol) in THF was transferred to the flask containing the NaH under nitrogen using a double ended needle. The resulting suspension was stirred for 36 h at room temperature. This MgH_2 slurry was used in the experiments involving anhydrous $CoCl_2$.

Preparation of alkyne hexacarbonyl dicobalt complex and the Pauson–Khand reaction with norbornene

To a magnetically stirred suspension of $CoCl_2$ (15 mmol) in THF (60 ml), MgH_2 (~ 15 mmol) slurry in THF (60 ml) was added during 20 min at 0 °C (ice bath) with carbon monoxide bubbling through, and the mixture was then stirred for 2 h. 1-Decyne (7.5 mmol) was added followed by norbornene (20 mmol). The stirred mixture was heated at 70–80 °C for a further 6 h under carbon monoxide then cooled to room temperature and poured into water (100 ml). The precipitate was filtered off and the two phases were separated. The aqueous phase was extracted with ether. The combined organic extract was washed successively with water and brine then dried over anhydrous $MgSO_4$. The solvent was evaporated and the dark residue was subjected to chromatography on a silica gel column. Hexane eluted the coloured metal carbonyl derivative, and 5% ethyl acetate in hexane eluted the Pauson–Khand ketone **1** in 66% yield. IR (neat): 2950, 1700, 1150–1000 (broad) cm^{-1}; ^1H NMR: δ 7.0 (br, 3H), 2.5 (br), 2.3 (br), 2.1 (br, 3aH, 4H, 7H, 7aH), 1.6–1.1 (m, 5H, 6H, 8H and alkyl protons); 0.8 (br, t, CH_3); ^{13}C NMR: δ 209.3 (C_1), 157.2 (C_3), 148.8 (C_2), 52.9, 47.2, 38.1, 37.3, 31.1, 30.1, 28.5, 27.1, 23.9, 21.8, 13.3; MS (*m/e*): 260 (M^+, 50%), 232 (10%), 163 (100%), 162 (40%).

The above procedure was followed for the reaction using phenylacetylene in the place of 1-decyne. The ketone **2** was isolated in 53% yield. m.p. 92–94 °C, Lit. [9] 93–95 °C; IR (KBr): 3010, 2950, 1700, 1610 cm^{-1}; ^1H NMR: δ 7.7–7.5 (m, 3H and some phenyl protons), 7.4–7.1 (m, remaining phenyl protons), 2.6 (br, 3aH), 2.5–2.1 (m, 4H, 7H and 7aH), 1.7–1.1 (m, 5H and 6H), 1.1–0.9 (m, 8H); ^{13}C NMR: δ 208.8 (C_1), 160.0 (C_3), 144.7 (C_2), 131.3, 128.5, 128.1, 127.3, 126.7, 54.5, 47.2, 39.0, 37.9, 30.8, 28.7, 28.0; MS (*m/e*): 224 (M^+, 100%), 196 (10%), 158 (75%), 156 (60%); Anal. found: C, 85.43; H, 7.17. $C_{16}H_{16}O$ calcd.: C, 85.6; H, 7.14%. The ^1H NMR spectral data agree precisely with those previously reported [9].

In the run with 4-octyne the desired cyclopentenone derivative **3** was isolated in 27% yield. IR (neat): 1700, 1640, 1350, 1100 cm^{-1}; ^1H NMR: δ 2.5–1.9 (m, 3aH, 4H, 7H and 7aH), 1.6–1.1 (m, 5H, 6H and 8H), 1.0–0.7 (m, alkyl protons); ^{13}C NMR: δ 210.8 (C_1), 174.4 (C_3), 143.7 (C_2), 53.3, 50.0, 38.6, 37.1, 31.3, 31.0, 29.0, 28.5, 25.0, 21.7, 20.8, 14.1, 14.0; MS (*m/e*): 232 (M^+, 40%), 217 (100%), 204 (10%), 189 (30%).

From the reaction with diphenylacetylene, the ketone **4** was isolated in 40% yield. mp. 129–130 °C, Lit. [9] 130–131 °C; IR (KBr): 3050, 2950, 1700, 1600, 760, 700 cm^{-1}; ^1H NMR: δ 7.3–7.0 (m, phenyl protons), 3.1 (br), 2.5–2.3 (m), 2.0 (br, 3aH, 4H, 7H and 7aH), 1.6–0.8 (m, 5H, 6H and 8H); ^{13}C NMR: δ 209.1, 171.1, 134.9, 132.4, 129.6, 129.5, 128.7, 128.5, 127.9, 53.8, 50.5, 39.2, 38.0, 31.3, 29.6, 29.0. The ^{1}H NMR spectral data agree precisely with those previously reported [9].

Preparation of $NaCo(CO)_4$ reagent by the reduction of $CoBr_2$ or $CoCl_2$ in THF with sodium / naphthalene under carbon monoxide

Naphthalene (10 mmol), freshly cut sodium (33 mmol), and THF (60 ml) were placed in a three-necked round-bottom flask under N_2 atmosphere. As soon as the green colour started to form (5 min), anhydrous cobalt bromide (10 mmol) was added, with carbon monoxide bubbling through, and the mixture was stirred for 3 h at room temperature under CO. The IR spectrum of the solution was then recorded, and showed the exclusive formation of $Co(CO)_4^-$, (strong absorption at 1890 cm^{-1}). The metal carbonylate anion generated in this way was used for cyclization of dibromides **5** and **6**.

Cyclization using $NaCo(CO)_4$

$NaCo(CO)_4$ (10 mmol), in THF (60 ml) was prepared by the procedure given above. 1,2-bis(bromomethyl)benzene **6** (5 mmol) was added and the mixture refluxed for 8 h under carbon monoxide then added water (20 ml). Sodium chloride was added and the organic layer was extracted with ether (3 × 30 ml). The organic layer was washed with brine dried over anhydrous $MgSO_4$ and evaporated. The residue was subjected to column chromatography and 2-indanone **8** was isolated in 46% yield. IR (neat): 3050, 2900, 1745 cm^{-1}. ^{13}C NMR: δ 214.8, 138.5, 128.0, 125.5, 44.0. The cyclization of dibromide, **5** to **7** was carried out similarly. Yield: 66%. IR (KBr): 3050, 2900, 1700 cm^{-1}. ^{1}H NMR: δ 7.1–7.5 (m, 8H), 3.4 (s, 2H). ^{13}C NMR: δ 209.9, 138.9, 132.7, 129.1, 129.0, 127.7, 127.4, 48.7.

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