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A SIMPLE METHOD FOR THE SPECIFIC SYNTHESIS OF MONOSUBSTITUTED DERIVATIVES OF THE GROUP VI METAL HEXACARBONYLS

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SUMMARY

Halopentacarbonylmetallates of Group VI react with ligands, L, in the presence of a Lewis acid to give $LM(CO)_5$ ($M = Cr$, Mo, W) in high yield under mild conditions.

INTRODUCTION

Direct reaction between a Group VI metal carbonyl, $M(CO)_6$, and a ligand, L, may in a certain restricted number of cases, lead to $LM(CO)_5$ as the sole product, but in the majority of other cases this is not true. Indirect methods, in which the ligand L should displace another ligand (not CO) from a "labile" complex are not necessarily more successful. This is demonstrated by the reactions of the anions $[(CO)_5MX]^-$ ($M = Cr$, Mo, W; $X =$ halogen) with diamines, isonitriles, and monophosphine which lead to *cis*-$L_2M(CO)_4$ as the major product in every case. A further disadvantage of such indirect methods is the difficulty which is often experienced in preparing the "labile" precursor complex such as $THF \cdot Cr(CO)_5$ for example[1]. The hydride ion catalysed substitution reaction between $M(CO)_6$ and L leads to $L_2M(CO)_4$ as the sole product in almost every case[2].

DISCUSSION

The method which is exemplified here has the advantages of high specificity, high yield, broad generality and, not least important, experimental simplicity. The addition of the ligand, L, which may be any conventional donor such as an amine, nitrile, isonitrile, phosphine or phosphite, either neat or as a solution in CH_2Cl_2, to an equimolar solution of the readily available halopentacarbonylmetallate salt, $R_4N[(CO)_5MX]$ ($R = Me$, Et; $M = Cr$, Mo, W; $X = Cl$, Br, I)[3], in the same solvent at or just below room temperature is followed immediately by the addition of a Lewis acid. The acids we have used include Et_3OBF_4, $AgNO_3$, $AgBF_4$ and $AlCl_3$. The reaction which follows the addition of the acid is fast, usually being complete in a few seconds. The yield of $LM(CO)_5$ is essentially quantitative and pure compounds can usually be isolated in yields of over 80 per cent.

When a potentially chelating bidentate ligand such as $(R_2ECH_2)_2$ ($R = Me$;

$E = N,P$) is used in the reaction the product is monodentate $(CO)_5MER_2CH_2CH_2ER_2$, thus indicating a general synthetic method for mono-*hapto* polydentate compounds of this type of which very few examples are known at present[4].

Kinetic data for the reaction $L_xM(CO)_y + L' \rightarrow L_xL'M(CO)_{y-1}$ have indicated[5] that the reaction proceeds through a pseudo-radical intermediate, $L_xM(CO)_{y-1}$ (*e.g.* $(CO)_5Cr\cdot$). This intermediate is produced in the rate-determining step which is usually slow and therefore allows time for side reactions to intervene; the formation of the intermediate is succeeded by a fast reaction with L′. We suggest that in the method described here, the intermediate $[(CO)_5Cr]$ is produced as a transient species in a fast reaction: it is then captured by the ligand to give $L'Cr(CO)_5$.

EXPERIMENTAL

For the purposes of brevity the following account refers to the chromium series only and specifically to the use of $Et_4N[(CO)_5CrCl]$, (I), as a starting material. It should be pointed out, however, that we have employed the reaction with equal success in systems containing molybdenum and tungsten. The salt (I)[3], triethyloxonium fluoroborate[6], Me_2CHNC[7], Me_3PAgNO_3[8] and $(Me_2PCH_2)_2$[9] were prepared by standard methods. Other materials were of reagent grade. All reactions were carried out in dioxygen-free dinitrogen. Melting points (Koffler block) are uncorrected. Infrared spectra were recorded in hexane or CH_2Cl_2 solution using a PE 257 grating spectrometer. NMR spectra were obtained with a PE R12 instrument at 60 MHz. Products were characterised by comparison of their melting points and infrared spectra with values from the literature. New compounds were characterised more fully. In all cases, no evidence was found for the formation of $L_2Cr(CO)_4$ or $L_3Cr(CO)_3$. The yields refer to pure isolated $LCr(CO)_5$ compounds.

1. *Acetonitrile.* The salt (I) (0.40 g, 1.09 mmole) was dissolved in pure dry CH_2Cl_2 (10 ml) contained in a 100 ml Schlenk tube and acetonitrile (2 ml excess) was added. Et_3OBF_4, (II), (0.30 g, excess) dissolved in CH_2Cl_2 (10 ml) was added to the magnetically stirred solution. An orange colouration developed which disappeared within a few seconds to give a yellow-green solution. All volatile material was removed under reduced pressure and the residue extracted with hexane/ether (2/1 v/v). Crystallisation of this solution at −20° gave yellow needles of $MeCNCr(CO)_5$ (0.23 g; 90% based on (I); m.p. 69–70°; ν 2281 vw, 2076 m, 1988 vw, 1953 vs, 1928 s cm^{-1}. Lit.[1] m.p. 71°, yield 57%; ν 2076 m, 1988 vw, 1953 vs, 1928 s cm^{-1}). The effect of varying the Lewis acid upon the yield of $MeCNCr(CO)_5$ in this reaction under otherwise identical conditions was as follows: $AlCl_3$(71%), $AgNO_3$(85%), $AgBF_4$(92%).

2. *Ammonia.* The salt (I) (0.25 g, 0.7 mmole) was dissolved in CH_2Cl_2 (10 ml) contained in a 100 ml Schlenk tube and the resulting solution cooled to ca. −30°. Excess liquid NH_3 was added, followed immediately by excess (II) dissolved in CH_2Cl_2 (10 ml). A yellow precipitate formed immediately. Volatiles were removed under reduced pressure and the residue was suspended in water and filtered. The residue was washed with water until the washings were colourless. The yellow solid remaining was dried *in vacuo* to give $NH_3Cr(CO)_5$ (0.14 g, 91%; m.p. ca. 150° (dec.); ν(CO) 2056 w, 1977 m, 1933 vs, 1890 s cm^{-1}. Lit.[1] m.p. 150° (dec.), yield 70%; ν(CO) 2065, 1980, 1935, 1885 cm^{-1}).

3. *Monophosphine.* The addition of water to solid $Mg[Al(PH_2)_4]_2$ produced

monophosphine which was then allowed to bubble through ice-cold CH_2Cl_2 (10 ml) until a saturated solution was obtained. The salt (I) (0.33 g, 0.92 mmole) dissolved in CH_2Cl_2 (10 ml) was added to the saturated solution of monophosphine followed immediately by a solution of (II) (0.2 g, excess) in the same solvent. The whole experiment was performed in the shade. The resulting solution was stirred for 5 minutes after which the volatiles were removed under reduced pressure. The residue was extracted with hexane/ether (3/1 v/v) and crystallisation of the solution at $-20°$ produced pale yellow crystals of $PH_3Cr(CO)_5$ (0.19 g, 92%, m.p. 113–114°; ν_{max} 2340 vw, 2077 w, 1986 vw, 1958 s, 1928m cm^{-1}. Lit.[1]: m.p. 116°, yield 10%; ν_{max} 2358, 2075 m, 1982 sh, 1953 vs, 1924 m cm^{-1}).

4. *Trimethylphosphine.* The salt (I) (0.44 g, 1.2 mmole) was dissolved in CH_2Cl_2 (10 ml) and to the solution was added Me_3PAgNO_3 (0.30 g, 1.3 mmole) dissolved in CH_2Cl_2 (5 ml). A white precipitate formed immediately which darkened rapidly on exposure to light. The solvent was removed under reduced pressure and the residue was then extracted with hexane/ether (1/1 v/v). Crystallisation of this solution at $-20°$ produced colourless needles of $Me_3PCr(CO)_5$ (0.29 g, 90%; m.p. 57–58° (dec.); ν_{max} 2064 w, 1952 m, 1941 vs cm^{-1}; Lit.[1]: m.p. 59°, yield "almost" quantitative; ν_{max} 2064, 1952, 1941 cm^{-1}).

5. Using the same procedure as that described in 1 above, the following compounds were also prepared: (a) $Me_2CHNCCr(CO)_5$ pale yellow needles, 82%. (m.p. 47–48°; ν_{max} 2158 m, 2065 m, 1960 vs cm^{-1}; lit.[10] m.p. 47–48°, yield 64%; ν_{max} 2158, 2065, 1960 cm^{-1}). (b) $(MeO)_3PCr(CO)_5$ colourless needles, 89%. (m.p. 0–5°; ν_{max} 2071 m, 1963 s, 1948 s cm^{-1}; lit. liquid product, 30%; ν_{max} 2073, 1885. 1963. 1948 cm^{-1}).

6. *N,N,N',N'-Tetramethylethylenediamine.* The same procedure as in 1 above was used to give yellow needles of the new complex $Me_2NCH_2CH_2NMe_2Cr(CO)_5$ which decomposed without melting at ca. 90°. The yield was 65%: (Found: C, 39.9; H, 5.0; Cr, 16.0, N, 10.0, $C_{11}H_{16}CrN_2O_5$ calcd.: C, 42.8; H, 5.2; Cr, 16.9; N, 9.1%.) The compound decomposes quite rapidly in hydrocarbon solvents at room temperature to give $Cr(CO)_6$, but the following infrared spectrum can be obtained in hexane ν(CO) 2068 w, 1935 s, 1918 m cm^{-1}.

7. *P,P,P',P'-Tetramethylethylenediphosphine.* The same procedure as in 1 above was used to give pale yellow needles of the new complex $Me_2PCH_2CH_2PMe_2$-$Cr(CO)_5$ (m.p. 122–123°, 72% yield. Found: C, 38.3; H, 4.9; Cr, 14.5. $C_{11}H_{16}CrO_5P_2$ calcd.: C, 38.6; H, 4.7; Cr, 15.2%). IR spectrum ν(CO) 2063 w, 1950 m, 1938 vs cm^{-1}. NMR spectrum (C_6D_6, internal TMS) δ 0.79 (6H, d, ^2J(PCH) 3.1 Hz), 0.88 (6H, d, ^2J(PCH) 7.6 Hz), 1.29 (4H, m) ppm.

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