

Preliminary communication

The preparation and synthetic utility of some transition metal carbonyl Grignard reagents

JAMES M. BURLITCH and SIMON W. ULMER

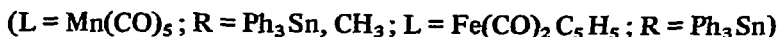
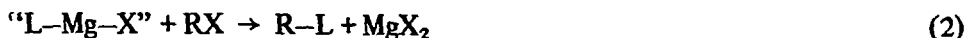
Department of Chemistry, Cornell University, Ithaca, N.Y. 14850 (U.S.A.)

(Received July 23rd, 1969)

The use of anionic transition metal carbonyls in the synthesis of organometallic derivatives has been well established¹. A common procedure employs the reduction of a dimeric metal carbonyl derivative, L-L (L = Co(CO)₄, Fe(CO)₂C₅H₅, Mn(CO)₅, Mo(CO)₃C₅H₅, etc.) or a metal carbonyl halide, L-X (X = Cl, Br, I) with 1% sodium amalgam and reaction of the resulting anionic species, L⁻, with a suitable substrate such as an organic or organometallic halide. The main disadvantages of this procedure are that large scale preparations require an inordinate amount of mercury and in some cases mercury derivatives are produced as side products².

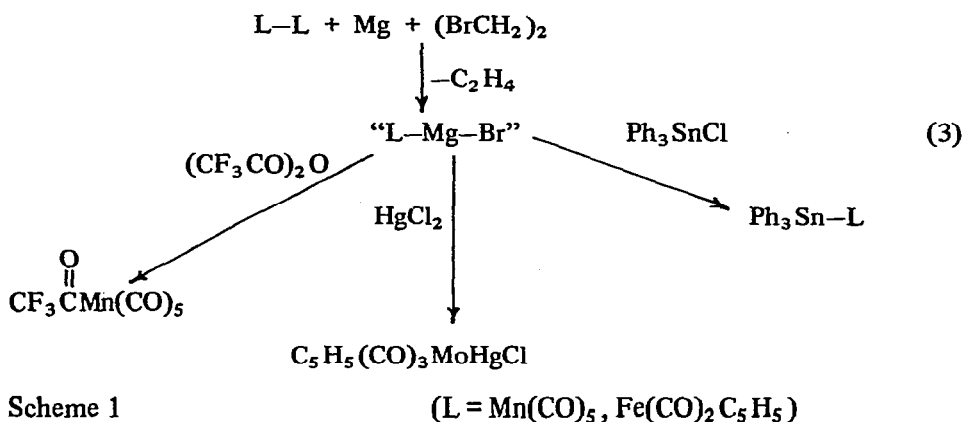
As an extension of our studies of the chemistry of transition metal carbonyl derivatives of the main group elements we have prepared some inorganic analogs of Grignard reagents which we tentatively formulate as "L-MgBr" (L = Mn(CO)₅, etc.) that have considerable potential as synthetic intermediates. We are prompted to present these results at this time by the recent disclosure of the isolation and characterization of two examples of this class of compounds *viz.* BrMgM(CO)₃C₅H₅(THF)_x (M = Mo, W)³.

Analogous to the well known behavior of organic halides, BrMn(CO)₅ and ClFe(CO)₂C₅H₅ react directly with an excess of magnesium metal (80 mesh) in tetrahydrofuran (THF) at room temperature to give highly colored, air sensitive solutions. Addition of triphenyltin bromide followed by hydrolysis of the mixture with saturated aqueous NH₄Cl solution afforded Ph₃SnMn(CO)₅ and Ph₃SnFe(CO)₂C₅H₅, isolated in 84 and 70% yields respectively. Similarly, addition of methyl iodide to "(CO)₅MnMgBr" produced CH₃Mn(CO)₅ in 90% yield as indicated by quantitative infrared analysis of the hydrolyzed reaction mixture. Separation of the product from the THF was hampered by the high volatility of the former. The processes involved in the foregoing transformations may be represented by the following



A second route to the Grignard reagent analogs parallels the "insertion" of zinc and cadmium into the Mn-Mn bond of Mn₂(CO)₁₀⁴. Thus when two mmoles each of

$\text{Mn}_2(\text{CO})_{10}$ and $\text{BrCH}_2\text{CH}_2\text{Br}$ were stirred with 6 mg-atoms of magnesium in 25 ml of THF at a gentle reflux in an argon atmosphere, the solution gradually changed from light yellow to deep burgundy in color over a 5 h period. After an additional 15 h 4 mmoles of Ph_3SnCl was added and stirring was continued at ambient temperature for 1 h. The mixture was hydrolyzed with 50 ml of saturated NH_4Cl , washed with three 50 ml portions of sat. NaCl , dried (MgSO_4) then evaporated. Recrystallization of the crude product from n-hexane afforded $\text{Ph}_3\text{SnMn}(\text{CO})_5$ in 75% yield. Likewise $\text{CF}_3\text{COMn}(\text{CO})_5$ was isolated in 79% yield by the addition of trifluoroacetic anhydride to “ $(\text{CO})_5\text{MnMgBr}$ ” formed by the above procedure. In an entirely analogous manner $\text{Ph}_3\text{SnFe}(\text{CO})_2\text{C}_5\text{H}_5$ (72%) was obtained from the reaction of $[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ with Mg and 1,2-dibromoethane. Unfortunately, this insertion reaction could not be applied to the production of $\text{Co}(\text{CO})_4$ derivatives from $\text{Co}_2(\text{CO})_8$ since the latter is rapidly decomposed by MgBr_2 in THF. When $[\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]_2$ was employed in the above procedure a light yellow, highly air sensitive intermediate was formed cleanly but no reaction occurred upon addition of Ph_3SnCl . In a separate experiment, however, the addition of one mole of HgCl_2 per mole of “ $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{MgBr}$ ” afforded $\text{C}_5\text{H}_5(\text{CO})_3\text{MoHgCl}$ in essentially quantitative yield. Scheme 1 summarizes these results. The observation that $\text{Ph}_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_5$ did not

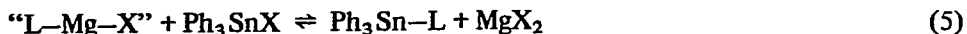


Scheme 1

form in this system is not surprising insofar as the compound isolated by Carrick and Glockling³ was produced from $\text{Et}_3\text{GeMo}(\text{CO})_3\text{C}_5\text{H}_5$ and excess MgBr_2 in a process analogous to the reverse of eqn. 2.

A third route to the L-Mg-X compounds is based on the ability of Group II metals to undergo metal-metal exchange reactions with transition metal derivatives of mercury previously demonstrated for Zn and Cd⁵. When a THF solution of $(\text{CO})_5\text{MnHgBr}$ ⁶ was stirred with an excess of magnesium for two hours at ambient temperature a light yellow, highly air sensitive solution was formed. Addition of Ph_3SnCl and subsequent workup afforded $\text{Ph}_3\text{SnMn}(\text{CO})_5$ in 93% yield. Of the three methods this metal exchange route gave the cleanest preparation of “ $(\text{CO})_5\text{MnMgBr}$ ”. The analogous cobalt-mercury derivative, $(\text{CO})_4\text{CoHgBr}$ ⁷ could also be used to prepare “ $(\text{CO})_4\text{CoMgBr}$ ” although this reagent did not convert Ph_3SnCl completely to $\text{Ph}_3\text{SnCo}(\text{CO})_4$. Previous work⁸ in this laboratory has shown that nucleophiles such as bromide ion can displace transition metal carbonyl anions that are relatively weak

nucleophiles from main group metals. Thus in the sequence the process depicted by eqn. 5 may be partially or completely reversed depending on the relative nucleophilic character of



M⁺ and X⁻. As noted previously, this phenomenon is probably responsible, at least in part, for the failure to form Ph₃SnMo(CO)₃C₅H₅ from "C₅H₅(CO)₃MoMgBr". Other factors, of necessity, must be involved since the nucleophilicities of Mn(CO)₅⁻ and C₅H₅Mo(CO)₃⁻ were found to be comparable as measured by the rate of displacement of I⁻ from an organic iodide⁹. In view of the large number of mercury halide derivatives that are accessible through direct reaction of transition metal carbonyls with mercuric halides¹⁰, the conversion of the L-Hg-X compounds to the much more reactive "L-Mg-X" intermediates should considerably expand their chemical reactivity. We are currently investigating the nature of these magnesium compounds in solution and in the solid state. Preliminary results suggest that considerable covalent character exists in the Mg-to-transition metal bond. Other reactions analogous to those of organomagnesium reagents are under study and complete details will be presented in a subsequent paper.

ACKNOWLEDGEMENTS

We are pleased to acknowledge financial support of this work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, as well as generous gifts of chemicals from Ethyl Corporation and Climax Molybdenum Company.

REFERENCES

- 1 For a review see R.B. King in F.G.A. Stone and R. West (Eds.), *Advances in Organometallic Chemistry*, Vol. 2, Academic Press, New York, 1964, p. 157.
- 2 R.B. King, *J. Inorg. Nucl. Chem.*, 25 (1963) 1296.
- 3 A. Carrick and F. Glockling, *J. Chem. Soc., A*, (1968) 913.
- 4 J.M. Burlitch, *Chem. Commun.*, (1968) 887.
- 5 J.M. Burlitch, *J. Organometal. Chem.*, 9 (1967) P9.
- 6 W. Hieber and W. Schropp, Jr., *Chem. Ber.*, 93 (1960) 455.
- 7 F. Bonati, S. Cenini and R. Ugo, *J. Chem. Soc., A*, (1967) 932.
- 8 J.M. Burlitch, *J. Amer. Chem. Soc.*, 91 (1969) 4562.
- 9 R.E. Dessy, R.L. Pohl and R.B. King, *J. Amer. Chem. Soc.*, 88 (1966) 5121.
- 10(a) H. Hock and H. Stuhlmann, *Chem. Ber.*, 61 (1968) 2097.
 (b) R.S. Nyholm and K. Vrieze, *J. Chem. Soc.*, (1965) 5337.
 (c) C.W. Bradford, W. van Bronswyk, R.J.H. Clark and R.S. Nyholm, *ibid. A*, (1968) 2456.
 (d) A.A. Chalmers, J. Lewis and S.B. Wild, *ibid.*, (1968) 1013.