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Reduction of Metal Carbonyls with Alkali Metal Carbides

MARK C. MANNING and WILLIAM C. TROGLER*
Department of Chemistry, Northwestern University, Evanston, Ill. 60201, U.S.A.

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The reaction of Na_2C_2 *and* Li_2C_2 *with* $Mn(CO)_5Br$ *yields* $Mn_2(CO)_{10}$*. The neutral complex* $Co_4(CO)_{12}$ *has been reduced to the* $Co_6(CO)_{14}^{4-}$ *cluster complex with* Na_2C_2*. A similar reaction with* $Fe_3(CO)_{12}$ *yielded* $[N(C_2H_5)_4][HFe_3(CO)_{11}]$ *upon addition of a methanol solution of* $[N(C_2H_5)_4]Br$*. These reactions may be carried out at room temperature and in tetrahydrofuran solvent.*

Introduction

Reagents with a wide range of capacities for the reduction of organic substrates have been available for quite some time [1]. The same cannot be said for the area of organometallics, especially in the formation of metal carbonyl clusters. Base induced disproportionation was one of the earliest routes to these species [2–4]. This procedure has been expertly exploited in the synthesis of a variety of rhodium and platinum carbonyl cluster anions [2, 5, 6]. The possible instability and insolubility of certain clusters, in basic media imposes some restrictions on the generality of this method. Another widely used method of redox condensation involves nucleophilic attack of a carbonylmetallate on either a neutral or cationic carbonyl compound [7, 8]. The first report of such a reaction was by Hieber ans Shubert (see Eqn. 1) [8].

$$Fe_3(CO)_{11}^{2-} + Fe(CO)_5 \xrightarrow[25\ ^\circ C]{THF} Fe_4(CO)_{13}^{2-} + 3CO \tag{1}$$

Gladfelter and Geoffroy have cleverly used this method to produce mixed metal clusters [9]. Reports of formation of metal carbonyl cluster anions using standard reducing agents are few. Most of the reductions found in the organometallic literature have employed alkali metal reagents or organomagnesium compounds. These strong reductants, however, tend to lead to metal–metal bond cleavage and CO loss, processes which ultimately lead to anions of low nuclearity [2, 10–12]. In addition, these reagents are often difficult to handle and prepare. Recently, borohydrides have been considered as possible alternatives in cluster synthesis [13].

Some preliminary work has been done with aromatic anions as reducing agents [14a]. A report has also been published utilizing KC_8 as a reducing agent for mononuclear carbonyl compounds [14b]. Recently, a convenient room temperature preparation of KC_8 has been communicated [14c].

While investigating the possibilities of preparing carbide (or diacetylide) complexes by metathesis reactions using sodium carbide, Na_2C_2, we discovered its utility as a 'mild' reducing agent in tetrahydrofuran solvent. Metal carbides are known to reduce simple metal halides and oxides at high temperatures (>700 °C) [15, 16]; however, these has been no report of their use in organometallic chemistry. Spanier and co-workers have demonstrated reductive coupling of diphenylchlorophosphine to tetraphenyldiphosphine employing CaC_2 at 70–150 °C [17–19]. The reducing properties of alkali metal carbides towards some organometallic systems will now be described.

Results and Discussion

The 'model' system investigated was the reductive coupling of bromopentacarbonyl manganese to $Mn_2(CO)_{10}$*. This reaction reaches completion (85% isolated yield) in four to six hours at room temperature and in tetrahydrofuran (THF) solvent. Product analysis establishes the complete stoichiometry of equation (2) (see Experimental Section). A number

$$2Mn(CO)_5Br + Na_2C_2 \xrightarrow{THF} Mn_2(CO)_{10} + 2NaBr + 2C(s) \tag{2}$$

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*Author to whom correspondence should be addressed.

*At the present time, the synthesis of $Mn_2(CO)_{10}$ from $Mn(CO)_5Br$ is not of practical utility since existing routes to the latter complex begin with $Mn_2(CO)_{10}$.

TABLE I. Reaction Conditions and Yields for Two Reductive Coupling Reactions which Employ Metal Carbides.

Carbide	RXN Time (hr)	RXN Temp (°C)	% Yield	Reference
$2Ph_2PCl \longrightarrow Ph_2PPPh_2$				
CaC_2	24	150	30	17
SrC_2	20	110	30	17
BaC_2	20	95	24	17
Na_2C_2	78	70	42	17
LaC_2	25	180	0	17
Al_4C_3	72	165	0	17
$2Mn(CO)_5Br \longrightarrow Mn_2(CO)_{10}$				
Na_2C_2	5	25	85	This work
Li_2C_2	72	50	38	This work
CsC_2	24	50	<1	This work

of reactions have been reported for the formation of $Mn_2(CO)_{10}$ which exhibit yields of 10–60% [20–26]. Most procedures employ high pressures of carbon monoxide as well as high temperatures. The only viable synthesis which did not involve high pressures, was a modification by King *et al.* of the method proposed by Calderazzo [27, 28]. This involved the reduction of $(C_5H_4CH_3)Mn(CO)_3$ by sodium suspended in refluxing diglyme under 1 atm of CO to form $Mn(CO)_5^-$. Subsequent hydrolysis with 85% H_3PO_4 yielded some $Mn_2(CO)_{10}$ (16–20%). Our attempts to reduce $(C_5H_4CH_3)Mn(CO)_3$ with sodium carbide under 1 atm of CO at room temperature did not yield any $Mn_2(CO)_{10}$.

The effect of varying the metal carbide employed in reaction (2) was studied. Borden and Spanier investigated a number of metal carbides in the reduction of diphenylchlorophosphine [19]. The yields and reaction parameters for their studies along with those we observed are given in Table I. Only alkali and rare earth carbides give reduction products. These compounds also exhibit the greatest ionic character, however; the trends cannot be entirely attributed to such tendencies. Lanthium carbide is quite ionic, but its pi-electron density is near that of a carbon–carbon double bond, and the active carbides have pi-electron density equivalent to that of a carbon–carbon triple bond [19]. Our limited observations tend to support these conclusions. It should be noted that attempts to increase the reactivity of the alkali metal carbides by the addition of crown ethers to the reaction medium were unsuccessful.

A mechanism for the reductive coupling of diphenylphosphine was proposed by Spanier and Caropreso [18], and postulates the formation of free radicals (see Eqns. 3, 4).

$$CaC_2 + 2Ph_2PCl \longrightarrow CaCl_2 + 2C + 2Ph_2P\cdot \qquad (3)$$

$$2Ph_2P\cdot \longrightarrow Ph_2PPPh_2 \qquad (4)$$

Inhibition of product formation in the presence of sulfur, a known free radical trap, was cited as evidence for this hypothesis. Subsequent work has shown that sulfur reacts directly with sodium carbide to form $Na_2(SCCS)$ [29], suggesting an alternative explanation for inhibition; however, a free radical mechanism is still plausible.

Bromomanganese pentacarbonyl undergoes an electrochemical two-electron reduction [30, 31]. Wrighton and Morse have found that compounds of the form $XML_2(CO)_3$ (X = Cl, Br, I; M = Mn, Re; L = CO, PR_3, N donors) undergo two-electron reductions both electrochemically and in the presence of sodium amalgam [32]. It would therefore seem likely that Na_2C_2 initially reduces $Mn(CO)_5Br$ to $Mn(CO)_5^-$ (Eqn. 5). The presence of $Mn(CO)_5^-$ was verified by monitoring the reaction using IR spectrometry. Low energy bands at 1899 and 1863 cm^{-1} are characteristic of this species [35].

$$Mn(CO)_5Br + Na_2C_2 \longrightarrow NaMn(CO)_5 + NaBr + 2C \qquad (5)$$

The mechanism of the subsequent reaction of $Mn(CO)_5^-$ with $Mn(CO)_5Br$ to form $Mn_2(CO)_{10}$ has not been determined. Wrighton and Morse concluded that simple nucleophilic displacement could not account for their observation of metal–metal bond formation [32]. A radical pathway could not be ruled out.

Sodium carbide was also found to reduce a number of larger carbonyl complexes. Combination with $Co_4(CO)_{12}$ over a period of four days at room temperature yields $Co(CO)_4^-$ (ν_{CO} 1890 cm^{-1}) and $Co_6(CO)_{14}^{4-}$ (ν_{CO} 2000, 1920, 1885, 1856 cm^{-1}), proceeding via the formation of $Co_6(CO)_{15}^{2-}$ (ν_{CO} 2044, 1982, 1958, 1783, 1734 cm^{-1}). This reaction had previously been carried out using sodium amalgam as the reducing agent and the infrared spectra agree with those reported for these compounds [33]. Metathesis of $Co_6(CO)_{14}^{4-}$ to the potassium salt yielded a product with an infrared spectrum identical to that previously reported [33].

The reaction between $Fe_3(CO)_{12}$ and Na_2C_2 was complete in twelve hours at room temperature. It did not proceed cleanly, giving $Fe(CO)_5$ and a mixture of cluster anions. Addition of a methanol solution of $[(C_2H_5)_4N]Br$ afforded $[(C_2H_5)_4N][HFe_3(CO)_{11}]$ in 38% isolated yield. The infrared spectrum was identical to that of an authentic sample prepared by unidentified alternate route [34]. Other carbonyl compounds were also present in the filtrate. Attempts to reduce $Fe(CO)_5$ did not prove successful.

Conclusions

Sodium carbide suspensions effectively reduce a number of metal carbonyl complexes in THF solution. Its reducing strength appears to be somewhat less than elemental sodium, and the solid powder is convenient to weigh and transfer. Since sodium carbide and the product graphite are both insoluble, separation from the reaction mixture is simple. We recommend that sodium carbide be added to the organometallic chemist's list of synthetically useful reducing agents.

Experimental

The carbides Na_2C_2, NaC_2H, Li_2C_2, and CaC_2 were used as received from Alfa, and ground to a fine powder under a nitrogen atmosphere before use. The carbonyls $(CH_3C_5H_4)Mn(CO)_3$ (Ethyl Corp.), $Mn_2(CO)_{10}$ (Alfa), $Mn(CO)_5Br$, $Fe_3(CO)_{12}$, and $Co_4(CO)_{12}$ (Strem) were used without further purification.

All manipulations were carried out under a nitrogen atmosphere employing standard Schlenk techniques. Tetrahydrofuran was freshly distilled from sodium/benzophenone into the reaction flask. All other solvents were reagent grade and degassed before use.

Reaction between Mn(CO)₅Br and Na₂C₂

The reaction flask was charged with 0.25 g (0.91 mmol) of $Mn(CO)_5Br$. Na_2C_2 was added in a greater than three-fold excess in an inert atmosphere glove box. After addition of THF (25 ml) the mixture was stirred for four hours and the solvent removed in vacuo. Infrared spectroscopy proved that no $Mn(CO)_5Br$ was present. The residue was extracted with hexanes (100 ml), and the solvent removed *in vacuo* to yield 0.16 g (0.39 mmol, 86%) of $Mn_2(CO)_{10}$ (identified by ir and mass spectra analysis). Further purification may be accomplished by vacuum sublimation at 50 °C. X-ray powder diffraction studies of the hexane insoluble residue established the presence of graphite and NaBr. Sodium carbide may contain acetylide impurities; however, we observed no $Mn_2(CO)_{10}$ when NaC_2H was substituted for Na_2C_2.

Reaction between Co₄(CO)₁₂ and Na₂C₂

This reaction was carried out as above, but with at least a fourfold excess of Na_2C_2. The solution initially turned green, indicative of $Co_6(CO)_{15}^{2-}$, and then red-brown after four days to give $Co_6(CO)_{14}^{4-}$ and $Co(CO)_4^-$ as the only products by infra-red spectroscopy. Attempts to isolate the anion as the $[(C_6H_5)_3P]_2N^+$ salt failed, and the potassium salt was the only isolable compound. The IR spectrum of the potassium salt was identical to that previously reported [33].

Reaction of Fe₃(CO)₁₂ with Na₂C₂

The flask was charged with 0.10 g (0.20 mmol) of $Fe_3(CO)_{12}$. Again, an excess of Na_2C_2 was added and the THF was distilled into the reaction vessel. After 12 hours of stirring, a number of new IR bands appeared. The reaction did not proceed cleanly. Some $Fe(CO)_5$ was identified and could be removed by high vacuum pumping. The only product to be isolated was $HFe_3(CO)_{11}^-$ as the $N(C_2H_5)_4^+$ salt. This was accomplished by adding a saturated methanol solution of $[N(C_2H_5)_4Br]$ to the solution and filtering. Yield 0.05 g, 38%. An attempt to reduce $Fe(CO)_5$ in the same manner did not show any reaction to occur after four days.

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