

SHORT COMMUNICATIONS

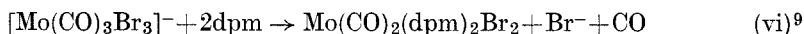
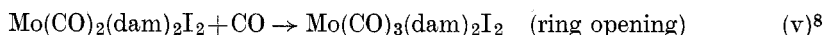
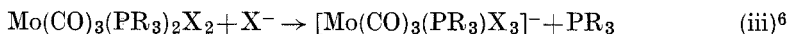
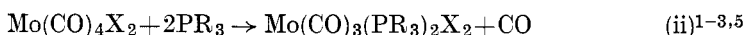
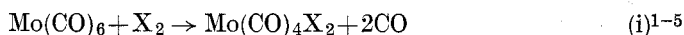
CARBONYL HALIDES OF THE GROUP VI TRANSITION METALS

XXII.* REACTION OF HALOPENTACARBONYL-CHROMIUM, -MOLYBDENUM, AND -TUNGSTEN(0) ANIONS WITH CARBON MONOXIDE

By J. A. BOWDEN† and R. COLTON†

[Manuscript received October 7, 1970]

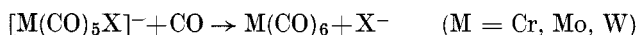
In earlier papers in this series, we have reported examples of a wide variety of substitution reactions found in the course of a study of the interaction of various ligands with the halocarbonyls of molybdenum and tungsten $M(CO)_4X_2$ ($X = Cl, Br, I$).



These examples show all possible combinations of replacement of halogen, phosphine or arsine, and carbon monoxide in substitution reactions except for the replacement of halide by carbon monoxide.

Many examples of substitutions similar to those listed above but involving molybdenum(0) and tungsten(0) have also been reported,^{10,11} but again no example of halogen replacement by carbon monoxide has so far been described.

In this paper we report that the reaction



proceeds smoothly at room temperature and pressure.

* Part XXI, *Aust. J. Chem.*, 1970, **23**, 2517.

† Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052.

¹ Colton, R., and Tomkins, I. B., *Aust. J. Chem.*, 1966, **19**, 1143.

² Colton, R., and Tomkins, I. B., *Aust. J. Chem.*, 1966, **19**, 1519.

³ Anker, M. W., Colton, R., and Tomkins, I. B., *Aust. J. Chem.*, 1967, **20**, 9.

⁴ Bowden, J. A., and Colton, R., *Aust. J. Chem.*, 1968, **21**, 2657.

⁵ Colton, R., and Rix, C. J., *Aust. J. Chem.*, 1969, **22**, 305.

⁶ Bowden, J. A., and Colton, R., *Aust. J. Chem.*, 1969, **22**, 905.

⁷ Anker, M. W., Colton, R., Rix, C. J., and Tomkins, I. B., *Aust. J. Chem.*, 1969, **22**, 1341.

⁸ Colton, R., and Rix, C. J., *Aust. J. Chem.*, 1970, **23**, 441.

⁹ Colton, R., and Howard, J. J., *Aust. J. Chem.*, 1969, **22**, 2543.

¹⁰ Abel, E. W., Butler, I. S., and Reid, I. G., *J. chem. Soc.*, 1963, 2068.

¹¹ King, R. B., *Inorg. Chem.*, 1964, **3**, 1039.

Experimental

Reaction Conditions

Carbon monoxide gas was bubbled through 10^{-3} – 10^{-4} M solutions of the tetraethylammonium salts of the halopentacarbonyl anions in A.R. chloroform at room temperature. The flow rate was kept constant throughout all the measurements so that the carbon monoxide pressure was 1 atm at all times.

Rate Measurements

The rates of the reactions were monitored by measurement of the rate of production of $M(CO)_6$. Standard solutions of $M(CO)_6$ were made in A.R. chloroform with concentrations spanning those expected to be produced in these reactions. It was found that the *height* of the very sharp carbonyl stretching mode near 2000 cm^{-1} was proportional to the concentration of hexacarbonyl. Thus

$$\begin{aligned}\text{rate of reaction} &= d[\text{hexacarbonyl}]/dt \\ &= dC_h/dt\end{aligned}\quad (1)$$

where t is the time and C_h is the concentration of hexacarbonyl.

Rate Order

In order to compare the relative rates of reaction of the different anions, it was convenient to establish the rate order with respect to the concentration of the halopentacarbonyl complex. In general

$$\text{rate of reaction} = k([M(CO)_5X^-])^n = k(C_a)^n \quad (2)$$

where k is the rate constant and C_a is the concentration of anion.

TABLE 1
VALUES OF RATE CONSTANT k FOR REACTION BETWEEN
[$M(CO)_5X^-$] ANIONS AND CARBON MONOXIDE

X	$10^3k\text{ (min}^{-1}\text{)}$		
	M = Mo	M = Cr	M = W
Cl	13.7 ± 4.3^a	6.2 ± 0.6	4.0 ± 0.4
Br	6.5 ± 0.7	5.0 ± 0.5	3.6 ± 0.4
I	3.6 ± 0.4	2.2 ± 0.7	0

^a The error in the rate constant for this particular reactive species is larger than usual due to side reactions.

Procedure

Three solutions of the $[Cr(CO)_5Br]^-$ complex were made, the concentrations of which were in the ratio 4:2:1. The initial rates were measured for each solution and they were found to be in the ratio 4.2:1.8:1.0. The reaction of the second sample of $[Cr(CO)_5Br]^-$ with carbon monoxide was taken to completion (total time about 194 min) and the plot of $\log[Cr(CO)_5Br^-]$ against time was linear. Similarly three solutions of $[W(CO)_5Cl]^-$ were made with the same concentrations as above and their initial rates were found to be in the ratio 3.7:2.0:1.1. It is clear therefore that the value of n in equation (2) is unity in the initial stages of the reaction, where most of the rate measurements were actually made, and also that the first-order rate law is maintained throughout the reaction. Hence

$$\begin{aligned}dC_h/dt &= kC_a \\ &= k(C_{a(\text{initial})} - C_h) \\ \ln(C_{a(\text{initial})} - C_h) &= kt + \ln C_{a(\text{initial})}\end{aligned}\quad (3)$$

The values of k , calculated from equation (3), may then be used to compare the relative reactivities of the $M(CO)_5X^-$ anions towards replacement of the halogen by carbon monoxide

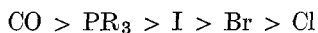
under identical conditions. These values are given in Table 1 together with an estimate of the errors. Each reaction was followed for at least 60 min to obtain these values.

Discussion

Extensive reactions of the $[M(CO)_5X^-]$ anions with nitrogen base ligands have been studied by Murdoch and co-workers (e.g.¹²). They found that there was competition between replacement of halide and replacement of carbon monoxide by the incoming ligand, which indicates a fine balance between the relative strengths of the metal-ligand bonds. In one reaction with an isonitrile, using what they termed "suitable conditions" (viz. carbon monoxide pressure), they stated that they removed traces of hexacarbonyl from the product by washing, but did not comment on the origin of the hexacarbonyl. We suggest that the hexacarbonyl was produced by reaction of the anion with carbon monoxide in competition with the isonitrile substrate. It is clear from our present results, and from the reactions that we reported in earlier papers, that the fine balance between relative strengths of metal-ligand bonds includes not only halogen and phosphine type ligands but also carbon monoxide.

As may be seen from Table 1, for a given metal the reactivity of the iodo anion is less than that of the bromo, which in turn is slightly less than that of the chloro anion. Similarly, for a given halogen, the tungsten anions are much less reactive than the chromium anions. These in turn are slightly less reactive than those of molybdenum, which is the usual order for the reactivities of the Group VI hexacarbonyls. Thus the least reactive anion would be expected to be $[W(CO)_5I^-]$ and, in fact, this was the only anion which showed no appreciable reaction with carbon monoxide at room temperature after 24 hr. Partial reaction could be induced at temperatures around 40° but even at this temperature the reaction with this anion is still extremely slow.

The order of reactivity of the anions of a particular metal containing different halogens is consistent with the known¹³ order of their *trans* effects:



The *trans* effect is described by Venanzi¹³ as the effect of a coordinated group L upon the rate of substitution reactions of the group Y opposite to L. One explanation of this effect, based on the formation of π -bonds, is that, as there is a substantial delocalization of electronic charge towards the directing bond because of the formation of a π -bond between metal ion and directing ligand, the position *trans* to it will provide the easiest point of attack by a nucleophilic reagent.

It would be expected, therefore, that when CO is *trans* to a series of other strong "*trans* effect" groups such as halogen atoms, then the order of the rate of replacement of the halogen atoms in the equivalent reaction would be expected to be opposite to the order of their *trans* effects, as we have observed.

Acknowledgment

The authors wish to express their gratitude to Climax Molybdenum Company, New York, for a generous gift of hexacarbonyls.

¹² Murdoch, H. D., and Henzi, R., *J. organomet. Chem.*, 1966, 5, 166.

¹³ Venanzi, L. M., *Chem. in Br.*, 1970, 4, 162.