denum are nearly in a plane, and oxygen and X groups (X = OH, OOH, Cl) occupy axial positions.

T. S. Srivastava, E. B. Fleischer[10]
Chemistry Department, The University of Chicago
Chicago, Illinois 60637

Mechanism of Oxidative Addition Reactions. Retention of Configuration in the Reaction of Alkyl Halides

Sir:

There is great current interest in the mechanism(s) of oxidative addition of molecules XY to square-planar d^8 complexes.[1] We have made several observations which give detailed information for the reaction of $Ir(CO)ZL_2$ (Z = Cl, I, SCN; L = $P(C_6H_5)_3$, $P(C_6H_5)_2$-CH_3) with certain alkyl halides.

We conclude (1) that these reactions occur in a one-step, concerted process without the formation of intermediates, and in the absence of solvents; (2) that retention of configuration results at the carbon center of the alkyl group; and (3) a trans addition with respect to the square plane can occur even with these restrictions.

These results are in agreement with the predictions made on the basis of orbital symmetry arguments[2] (Figure 1a and b). The iridium complexes used are well known to act as nucleophiles, or as Lewis bases, in their reactions.[3] The highest filled molecular orbitals are chiefly d orbitals of the metal.

The compounds $Ir(CO)(SCN)L_2$ were made from $Ir(CO)ClL_2$[4] by addition of $[(C_4H_9)_4N]SCN$ in dichloroethane solution and precipitated with methanol. CH_3SCN and CH_3Cl react very slowly at room temperature with these complexes. Mixing $Ir(CO)(SCN)L_2$ with CH_3I in the presence of a very large excess of SCN^- in dichloroethane solution yields only $Ir(CO)$-$(SCN)L_2(CH_3)I$. Similarly, $Ir(CO)ClL_2$, upon addition of CH_3I with excess Cl^-, gives only $Ir(CO)ClL_2$-$(CH_3)I$. The $Ir(CO)ClL_2(CH_3)Cl$ species are stable compounds and inert toward I^- substitutions on this time scale. These products were precipitated from solution with methanol and recrystallized for analysis from benzene–methanol. Infrared and nmr spectra of the products in solution prior to and after recrystallization were identical.

Solid $Ir(CO)ClL_2$ compounds were both found to react readily with CH_3I gas at room temperature. Similarly, the more reactive $Ir(CO)Cl[P(C_6H_5)_2CH_3]_2$ adds CH_3Br gas. Infrared and far-infrared analyses

(1) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966); A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1562 (1969); I. C. Donek and G. Wilkinson, *ibid.*, *A*, 2604 (1969); J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).
(2) L. Salem, *Chem. Brit.*, 449 (1969); R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970).
(3) D. F. Shriver, R. N. Scott, and D. Lehman, *Inorg. Chim. Acta*, **4**, 73 (1970).
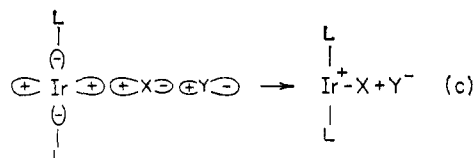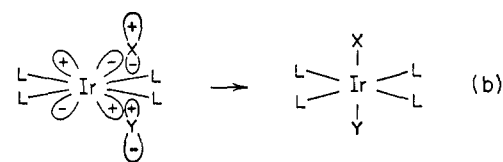(4) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **89**, 844 (1967).

Figure 1. (a) One-step cis addition; retention of configuration at X. (b) One-step trans addition; retention at X. (c) Two-step cis or trans addition; inversion at X.

of these products show they are identical with those found in solution. The product of CH_3Br addition has been shown by analysis of far-infrared Ir–Cl stretching frequency and nmr to be the result of trans addition.[5] By a similar analysis, the stereochemistry of both the products of CH_3I addition was also found to be the result of trans addition (ν_{Ir-Cl} = 300 cm^{-1} for both products).

Optically active $CH_3CHBrCOOC_2H_5$ ($[\alpha]^{25}D$ −6.0°) was obtained by resolution of $CH_3CHBrCOOH$[6] and conversion to the ester in HBr saturated ethanol. $Ir(CO)Cl[P(C_6H_5)_2CH_3]_2$ was stirred at room temperature with an equimolar amount of the ester in dichloromethane solution. The progress of the reaction was followed by the disappearance of the infrared carboxyl stretch of the free ester at 1742 cm^{-1} and the appearance of the coordinated ester carboxyl peak at 1698 cm^{-1}. After 4 days the solvent was evaporated and any remaining unreacted ester removed by repeated washings with pentane and pumping on the solid for 24 hr with a mercury diffusion pump. The product, $Ir(CO)$-$Cl[P(C_6H_5)_2CH_3]_2(CH_3CHCO_2C_2H_5)Br$, was found to be optically active, $[\alpha]^{25}D \sim -20°$. This complex was treated by slow addition of an equimolar amount of Br_2 in THF at −78° for 24 hr. An infrared spectrum of the product showed greater than 95% cleavage of the alkyl–metal bond to regenerate CH_3CHBr-$COOC_2H_5$. This ester in solution was removed from any remaining uncleaved complex by vacuum distillation. A rotation of $[\alpha]^{25}D \sim -4°$ was measured for this product.

Since no halide ions in solution are incorporated into the product, a one-step addition is indicated. The reaction of $Ir(CO)Cl[P(C_6H_5)_3]_2$ with CH_3I in the presence of $^{131}I^-$ is also known to show no ^{131}I in the product.[7] One-step addition is further indicated by

(5) J. P. Collman and C. T. Sears, *Inorg. Chem.*, **7**, 27 (1968).
(6) T. L. Rambert, *Justus Liebigs Ann. Chem.*, **349**, 324 (1906).
(7) P. B. Chock and J. Halpern, *Proc. Int. Conf. Coord. Chem., 10th 1967*, 135 (1967).

the facile addition of the alkyl halide gases where formation of ion intermediates can be excluded.

A one-step addition would require retention of configuration at the carbon atom. This has been confirmed by the addition and subsequent cleavage of optically active $CH_3CHBrCOOC_2H_5$. The regenerated bromoester has the same sign of rotation as the original. Thus two inversions or two retentions must be involved. Cleavage of alkyl-metal bonds with Br_2 is known to almost entirely occur with retention.[8] Thus the oxidative addition must also go with retention. In this case, however, because of the complexity of the ir spectrum, we were not able to decide if the addition was cis or trans.

A one-step addition of silicon hydrides to d^8 complexes has also been postulated.[9] In agreement with our work, Sommer has shown[10] that addition of silicon hydrides to $Ir(CO)Cl[P(C_6H_5)_3]_2$ occurs with retention of configuration at silicon.

Orbital symmetry considerations do not exclude a two-step mechanism for the reaction of d^8 complexes with alkyl halides (Figure 1c). A possible example, which goes with inversion of configuration at carbon, has been reported.[11]

Acknowledgment. The authors wish to acknowledge the valuable help of R. W. Johnson. Financial support came from the Atomic Energy Commission, Grant No. AT(11-1)-1087, and from a predoctoral NIH fellowship for W. R. M.

(8) F. R. Jensen and L. H. Gale, *J. Amer. Chem. Soc.*, **82**, 148 (1960); F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, **82**, 2466 (1960). R. W. Johnson (private communication) has shown that bromine cleavage of $CH_3CHCOOC_2H_5Mn(CO)_5$ occurs with retention of configuration.

(9) J. F. Harrod and C. A. Smith, *J. Amer. Chem. Soc.*, **92**, 2699 (1970).

(10) L. H. Sommer, J. E. Lyons, and H. Fujimoto, *ibid.*, **91**, 7051 (1969).

(11) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

(12) Address correspondence to this author.

Ralph G. Pearson,[12] Warren R. Muir
Department of Chemistry, Northwestern University
*Evanston, Illinois 60201*
Received June 23, 1970

Aromatic Electrophilic Substitution Reactions of Phenylmethylidynetricobalt Nonacarbonyl and Diphenylacetylenedicobalt Hexacarbonyl. Preparatively Useful Reactions of Coordinated Organic Ligands

Sir:

Electrophilic substitution reactions of π-bonded unsaturated organic ligands in transition metal complexes are well known[1] and such reactions can be valuable in organic synthesis when procedures are available for subsequent release of the organic ligand from the com-

(1) Some examples: (a) π-bonded cyclobutadiene in π-$C_4H_4Fe(CO)_3$: J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3254 (1965); (b) π-bonded cyclopentadienyl in ferrocene: R. B. Woodward, M. Rosenblum, and M. C. Whiting, *ibid.*, **74**, 3458 (1952); (c) π-bonded benzene in benzene–chromium tricarbonyl: R. Ercoli, F. Calderazzo, and E. Mantica, *Chim. Ind. (Milan)*, **41**, 404 (1959); R. Riemschneider, O. Becker, and K. Franz, *Monatsh. Chem.*, **90**, 571 (1959); (d) π-bonded cycloheptatriene and cyclooctatetraene in their iron tricarbonyl complexes: B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *Chem. Commun.*, 1273 (1969); B. F. G. Johnson, J. Lewis, A. W. Parkins, and G. L. P. Randall, *ibid.*, 595 (1969).

plex.[1a] Through our recent research in the area of carbon–cobalt cluster compounds,[2,3] we became interested in the possibility of organic transformations involving the ligands in compounds of types I and II.

or $ArCCo_3(CO)_9$ or $(ArC_2Ar)Co_2(CO)_6$

I   II
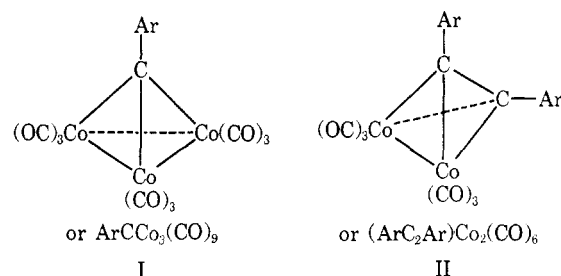
Both types of complexes are quite stable and easily prepared and handled (eq 1 and 2).[4]

$$ArC{\equiv}CAr + Co_2(CO)_8 \xrightarrow{(ref\ 4)} (ArC_2Ar)Co_2(CO)_6 + 2CO \quad (2)$$
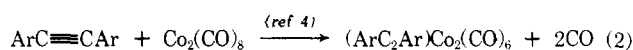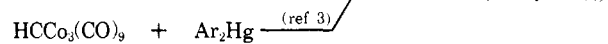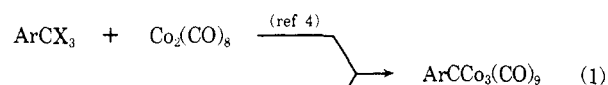
We have found that compounds of types I and II where Ar = phenyl undergo facile Friedel–Crafts acylation and that the organic ligands in the resulting products can be released from their cobalt complexes to give organic compounds in high yield. Such a reaction sequence is of special interest and utility in the case of $(PhC_2Ph)Co_2(CO)_6$ since Friedel–Crafts acylation of the free ligand, diphenylacetylene, cannot be accomplished directly. Both types of complexes, I and II, were found
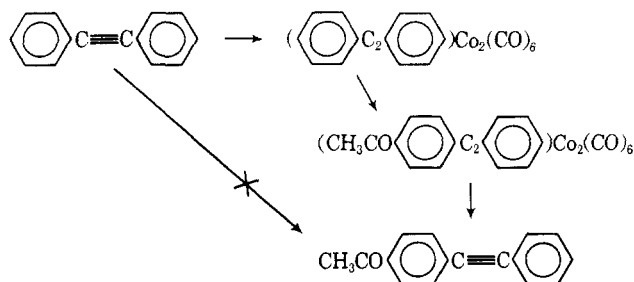
to be stable to the conditions of the Friedel–Crafts reaction and we have introduced acetyl, benzoyl, and formyl substituents in this manner (Schemes I and II).

The acetylation of phenylmethylidynetricobalt nonacarbonyl is described to illustrate the procedure used. A slurry of 5 mmol of anhydrous $AlCl_3$ in 50 ml of dichloromethane under argon was cooled to 0° and 5 mmol of acetyl chloride was added. The mixture was stirred at 0° for 10 min and then 5 mmol of $PhCCo_3$-$(CO)_9$ in 50 ml of dichloromethane was added. The reaction mixture was stirred at 0° for 15 min, at 25° for 2 hr, and subsequently poured onto ice water. Extraction of the aqueous phase was followed by drying and evaporation of the solvent Low-temperature crystallization of the residue from hexane gave 2.6 g (93%) of brown-black solid, mp 106–107°. A sample recrystal-

(2) D. Seyferth, R. J. Spohn, M. R. Churchill, K. Gold, and F. R. Scholer, *J. Organometal. Chem.*, **23**, 237 (1970).

(3) D. Seyferth, J. E. Hallgren, and R. J. Spohn, *ibid.*, in press.

(4) W. Hübel in "Organic Syntheses via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, pp 273–342.