

Recovery of the Cr(CO)₃ Unit in the Removal of Organic Ligands from their Chromium Carbonyl Complexes

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Summary A method is described for the removal of an organic ligand from its chromium carbonyl complex using pyridine (py) to give in high yields [(py)₃Cr(CO)₃]; the latter can be usefully recycled to make chromium carbonyl complexes.

THE activation of aryl rings towards nucleophilic attack via π -bonding co-ordination of a chromium tricarbonyl unit to the aromatic ring seems useful in synthesis.¹ However, the commercially available [Cr(CO)₃] necessary to make the complexes is very expensive. Moreover, once reaction with the complex is complete, removal of the chromium tricarbonyl group under conditions (iodine at 0 °C² or photochemical oxidation³) unlikely to interfere with other functional groups leads to destruction of the [Cr(CO)₃] unit to give, at best, products like CO₂ and Cr^{III} salts.

These facts indicate the limitations to a practical application of this potentially useful synthetic tool.

Now we have found that the removal of an organic ligand from its chromium tricarbonyl complex can be achieved in a general way, with a high percentage recovery of chromium as [(py)₃Cr(CO)₃] (py = pyridine), by reaction with refluxing pyridine.⁴ Also, the usefulness of [(py)₃Cr(CO)₃] in making chromium carbonyl complexes of organic ligands, in the presence of boron trifluoride-

diethyl ether in boiling ether, is quite general.^{5,†} The advantages (lower temperatures, shorter reaction times, and good yields) of this complexation method with respect to the use of [Cr(CO)₃] are more evident in connection with the removal of organic ligands by the above procedure.[‡]

In order to drive the decomplexation reaction to completion it is necessary to reflux the arene chromium tricarbonyl complex for 2 h with an eight—ten fold (by weight) excess of pyridine. Dilution with anhydrous ether and filtration gives directly the [(py)₃Cr(CO)₃] complex (for yields see Table). The free organic ligands were

TABLE. Results and conditions for removal of the ligand Ar from the chromium complexes [ArCr(CO)₃]^a

[ArCr(CO) ₃], Ar	% Yield of Ar ^b	% Yield of [(py) ₃ Cr(CO) ₃]
PhNEt ₂	90 ^c	98
Thiophen	70	78
PhCl	80	80
PhF	70	81
PhOMe	80 ^d	96
C ₆ H ₆	70	77
Naphthalene	75	70

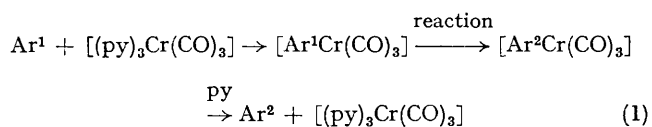
^a Reactions were carried under nitrogen at 115 °C for 2 h (but see note d). ^b Yields of ligand were determined gravimetrically (but see note c). ^c Yield of *NN*-dimethylaniline was determined by quantitative g.l.c. ^d Heating for 3 h.

† We have further checked the scope of this reaction by preparing the chromium carbonyl complexes of all the organic ligands listed in the Table.

‡ The use of readily available Lewis bases other than pyridine to accomplish the same reactions is under investigations, although first results do not seem encouraging.

purified from excess of pyridine by standard acid-base separation procedures. §

The advantages of this method of decomplexation are the relatively low temperature required ¶ (115 °C) and the use of chromium through the formal transfer of the π -bonded $[\text{Cr}(\text{CO})_3]$ unit from the modified final organic ligand Ar^2 to the starting ligand Ar^1 in the general sequence represented by equation (1).



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§ See also note c in the Table.

¶ Higher temperatures (160—180 °C) are necessary in the case of exchange of the aromatic ligand between arene tricarbonyl complexes and uncomplexed arenes; G. Natta, R. Ercoli, F. Calderazzo and E. Santambrogio, *Chim. and Ind.* (Milan), 1958, XL, 1003.

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² M. F. Semmelhack, H. T. Hall, M. Yoshifuji, and G. Clark, *J. Amer. Chem. Soc.*, 1974, **97**, 1247.

³ A. J. Birch, P. E. Cross, and H. Fitton, *Chem. Comm.*, 1965, 366; A. J. Birch, P. E. Cross, D. T. Conner, and G. S. R. Subba Rao, *J. Chem. Soc.*, 1966, 54; G. Jaouen and R. Dabard, *Tetrahedron Letters*, 1971, 1015.

⁴ $[(\text{py})_3\text{Cr}(\text{CO})_3]$ can be prepared by the reaction of tricarbonyl(*NN*-dimethylaniline)chromium with pyridine: D. E. F. Gracey, W. R. Jackson, W. B. Jennings, and T. R. B. Mitchell, *J. Chem. Soc. (B)*, 1969, 1204.

⁵ Some thiophen, selenophen, cycloheptatriene, and indene derivatives together with bromobenzene and iodobenzene have been complexed by this procedure; M. Novi, G. Guanti, and C. Dell'Erba, *J. Heterocyclic Chem.*, 1975, **12**, 1055; K. Öfele, *Chem. Ber.*, 1966, **99**, 1732; P. E. Baikie, O. S. Mills, P. L. Pauson, G. H. Smith, and J. Valentine, *Chem. Comm.*, 1965, 425.