Metal Atom Preparation and Ligand Displacement Reactions of Bisnaphthalenechromium and Related Compounds

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Summary Bisnaphthalenechromium or bis(1-methylnaphthalene)chromium, prepared from the ligands and chromium atoms, react under mild conditions with CO or $\mathrm{Bu^tNC}$ to form $[\mathrm{CrL_6}]$ and with $\mathrm{PF_3}$, $\mathrm{P(OMe)_3}$, or $\mathrm{PMe_3}$ to form $[\mathrm{Cr(naphthalene)L_3}]$ complexes; Mo, V, and Ti atoms also form exceptionally reactive complexes with naphthalene.

Naphthalene sandwich complexes containing a metal in the zerovalent state have been prepared previously only on a spectroscopic scale.[1] The reducing Friedel–Craft synthesis, although successful in the preparation of the cationic bisnaphthaleneruthenium(II)[2] complex, yields only partly hydrogenated naphthalene–chromium complexes with a composition approaching that of bistetralinchromium.[2,3] Using established metal vapour synthesis techniques,[4] we have found that chromium atoms react with naphthalene to give bisnaphthalenechromium and with 1-methylnaphthalene to give bis(1-methylnaphthalene)chromium. The latter is formed in a rotating solution reactor in yields up to 70% based on the chromium vaporized but ^{1}H n.m.r. spectroscopy shows it to be a mixture of isomers with either the $\mathrm{C_6H_3Me}$ or $\mathrm{C_6H_4}$ ring unit co-ordinated to the metal. The thermally stable, air sensitive, dark red-brown compounds bisnaphthalenechromium† [δ ($\mathrm{C_6D_6}$, $\mathrm{Me_4Si}$) 4·35 (m, 2H), 5·28 (m, 2H), and 6·92 (s, 4H)] and bis(1-methylnaphthalene)chromium† can be distinguished from all other reported bisarenechromium compounds by the lability of the co-ordinated arene rings. Whereas dibenzenechromium reacts with CO only at 300 atm and 200 °C,[5] bisnaphthalenechromium reacts smoothly with CO at 1 atm and 20 °C to give first $[\mathrm{Cr(C_{10}H_8)(CO)_3}]$[6] then $[\mathrm{Cr(CO)_6}]$. The lability of naphthalene in $[\mathrm{Cr(C_{10}H_8)(CO)_3}]$ has been observed earlier and is known to be an important factor in the catalytic properties of the compound.[7] Similarly, reaction of $[\mathrm{Cr(C_{10}H_8)_2}]$ with $\mathrm{Bu^tNC}$ in hexane gives $[\mathrm{Cr(Bu^tNC)_6}]$.[8] Reactions also occur under mild conditions with $\mathrm{PF_3}$, $\mathrm{P(OMe)_3}$, or $\mathrm{PMe_3}$ but only one co-ordinated naphthalene is displaced forming a $[\mathrm{Cr(C_{10}H_8)L_3}]$ complex. The lability of the naphthalene in these complexes to displacement by CO decreases in the order $\mathrm{L = PMe_3 > P(OMe)_3 > PF_3}$. I.r. studies show that $[\mathrm{Cr(C_{10}H_7Me)(PMe)_3}]$ yields a mixture of the known compounds $[\mathrm{Cr(PMe_3)_3(CO)_3}]$ and *cis*-$[\mathrm{Cr(PMe_3)_2(CO)_4}]$[9] with $[\mathrm{Cr(C_{10}H_7Me)(PMe_3)_2CO}]$ (ν_{CO} 1804 cm^{-1}) as the likely precursor of the latter compound.

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† These compounds gave satisfactory elemental (C, H) analyses.

We attribute the easy displacement of co-ordinated naphthalene compared with benzene to its lower aromatic delocalisation energy per ring.[10] The energy required to tilt the co-ordinated ring of naphthalene from being a six-electron donor to becoming a four-electron donor on demand from another ligand is substantially lower than for the analogous transition in benzene. Triphenylphosphine and triphenyl phosphite, unlike less bulky ligands, do not react under mild conditions with bisnaphthalenechromium, which suggests that only a limited tilting of the co-ordinated naphthalene can occur easily.

Molybdenum atoms also react efficiently with naphthalene or 1-methylnaphthalene to give stable but very air-sensitive complexes bisnaphthalenemolybdenum† [δ 4·72 (m, 2H), 5·04 (m, 2H), 6·58 (m, 2H), and 6·78 (m, 2H)] and bis(1-methylnaphthalene)molybdenum† which are analogous to those of chromium. As expected from the known greater reactivity of dibenzenemolybdenum compared with dibenzenechromium,[11] the co-ordinated naphthalene is displaced by CO or Bu^{t}NC faster at room temperature from bisnaphthalenemolybdenum than from bisnaphthalenechromium.

Vanadium atoms condensed into a cold solution of naphthalene in methylcyclohexane–tetrahydrofuran, yield a deep red, room-temperature-stable, air-sensitive compound analysing as bisnaphthalenevanadium. Its e.s.r. spectrum ($g = 1{\cdot}992$) is similar though not identical to that reported by Henrici[1] for the product of reduction of VCl_3 with lithium naphthalide in tetrahydrofuran. The naphthalene rings are again very labile and the compound promises to be an excellent starting material for preparing other zero-valent vanadium compounds. Condensation of titanium atoms with an excess of 1-methylnaphthalene followed by extraction with diethyl ether, yields a deep red solution, stable at 20 °C, which may contain a bisarenetitanium complex.[12]

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[1] G. Henrici and S. Olivé, *J. Organometallic Chem.*, 1967, **9**, 325; *J. Amer. Chem. Soc.*, 1970, **92**, 4831.
[2] E. O. Fischer, Ch. Elsenbroich, and C. G. Kreiter, *J. Organometallic Chem.*, 1967, **7**, 481.
[3] F. Hein and H. Kleinwachter, *Monatsber. Deut. Akad. Wiss. Berlin*, 1960, **60**, 607.
[4] P. L. Timms in 'Cryochemistry,' ed. M. Moskovits and G. A. Ozin, Wiley, New York, 1976, p. 61.
[5] E. O. Fischer and K. Öfele, *Chem. Ber.*, 1957, **90**, 2532.
[6] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Z. Naturforsch.*, 1958, **13b**, 458; *Chem. Ber.* 1958, **91**, 2763; G. Natta, R. Ercoli, F. Calderazzo and E. Santanbrogio, *Chimica e industria*, 1958, **40**, 1003.
[7] M. Cais, *Co-ordination Chem. Rev.*, 1975, **16**, 27; O. Iandolfi and M. Cais, *J. Organometallic Chem.*, 1977, **125**, 141.
[8] P. L. Timms and T. W. Turney, *J.C.S. Dalton*, 1976, 2021.
[9] R. Mathieu, M. Lenzi, and R. Poilblanc, *Inorg. Chem.*, 1970, **9**, 2030.
[10] M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw Hill, New York, 1969, p. 177.
[11] M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301.
[12] F. W. S. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J.C.S. Chem. Comm.*, 1973, 866.