Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Insertion into metal–carbon and hydrogen–carbon bonds; synthesis of Group VIA metal cyclopentadienylcarbonyl metallates and hydrides

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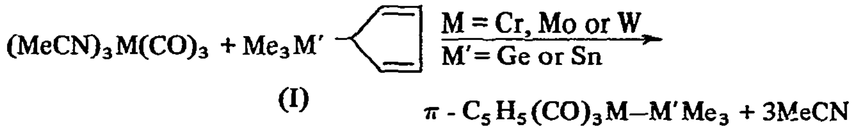
(Received July 30th, 1969)

A novel procedure (Eq.1) for the synthesis of compounds having metal–metal bonds is reported (see ref. 1 for earlier syntheses). This provides the first example of the insertion of a coordinatively unsaturated species into a metal–carbon σ-bond. There is formal similarity to reactions involving insertion into Group IV metal–halogen bonds[2]. Compounds (II), with two exceptions [II, M = Cr and M′ = Sn, m.p. 109°; II, M = Cr and M′ = Ge, m.p. 86–88°][3], have been described in the literature[4].



(1)

(II)

Preliminary examination, by NMR of the $Fe(CO)_5$/THF/$Me_3SnC_5H_5$ system at 20° suggests that π-$C_5H_5(CO)_2Fe{-}SnMe_3$ is formed. Reactions of type (1) may have a wider generality. The requirements may be that (*i*) the reagent (I), or more broadly LM″–X, is capable of functioning as a nucleophile by virtue of the nature of X (π-bond- or lone pair- possessing), (*ii*) the M″–X bond is labile, and (*iii*) that the product, such as (II), is thermodynamically stable. For reaction (1), reactivity decreases for M′ in (I) = Sn > Ge ≫ Si.

As a test of this hypothesis, the reagent LM″–X was next chosen to be cyclopentadiene, H–C_5H_5, Under controlled conditions (see Table 1), this system (Eq. 2) is probably the most convenient for synthesis of the important Group VIA π-cyclopentadienylcarbonyl hydrides. King and Fronzaglia[5] obtained the tungsten carbonyl hydride (32%) using reaction (2), and refluxing for several hours in n-hexane. The low yield was probably caused by thermal degradation of the hydride, although the choice of solvent is possibly significant.

$$(MeCN)_3M(CO)_3 + C_5H_6 \rightarrow \pi\text{-}C_5H_5(CO)_3MH + 3MeCN \qquad (2)$$

Further illustration is provided by the following example and Table 1.

TABLE 1

Reaction	M and M′	Optimal conditions (h/°)	Yield (%) [a]
Eq. 1	M = Cr, M′ = Sn	2/65 [b]	52
Eq. 1	M = Mo, M′ = Sn	6/65 [b]	75
Eq. 1	M = W, M′ = Sn	6/65 [b]	60
Eq. 1	M = Cr, M′ = Ge	2/65 [b]	10
Eq. 1	M = Mo, M′ = Ge	4/65 [b]	21
Eq. 1	M = W, M′ = Ge	4/65 [b]	49
Eq. 2	M = Cr	1/20 [c]	20
Eq. 2	M = Mo	½/50 [c]	65
Eq. 2	M = W	2/50 [d]	13
Eq. 2	M = W	16/69 [e]	32
Eq. 2	M = W	2/50 [c]	67

[a] % yield on M(CO)$_6$. [b] Refluxing THF as solvent; in CO atmosphere. [c] THF as solvent. [d] MeCN as solvent. [e] Refluxing n-C$_6$H$_{14}$ as solvent[5].

Hexacarbonylmolybdenum(0) (13.13 g, 49.7 mmoles) and degassed acetonitrile (50 ml) were heated together under reflux (16 h), in a nitrogen atmosphere. After cooling, the excess of acetonitrile was removed (20°/10^{-3} mm), and replaced by degassed tetrahydrofuran (25 ml). To the stirred yellow suspension was added an excess of freshly distilled cyclopentadiene (5 ml), and the mixture stirred (½ h/50°) in a nitrogen atmosphere, to form a brown solution. Solvent removal (20°/10^{-3} mm) and slow sublimation (40–80°/10^{-3} mm during 6 h) afforded yellow crystals of hydrido-π-cyclopentadienyltricarbonylmolybdenum(II) (7.95 g, 32.3 mmoles, 65% yield based on Mo(CO)$_6$).

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