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Preliminary communication

Variable site of Lewis basicity of π-$C_5H_5W(CO)_3^-$ in complexes with $(C_6H_5)_3In$ and $(C_6H_5)_3Al$

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The ability of transition metal carbonyl anions to form complex anions with closely related derivatives of main group metals has been reported recently[1]. In all of the compounds previously observed the site of Lewis basicity was the transition metal atom, and complexation occurred with the formation of additional metal–metal bonds. In this communication we report the first examples of Lewis acid-base complexes of metal carbonyl anions with organo-substituted main group elements and we present evidence which indicates that the site of Lewis basicity depends on the nature of the Lewis acid.

When dissolved with an equimolar amount of triphenylindium[2] in dichloromethane, π-$C_5H_5(CO)_3W^-N(n\text{-}Bu)_4^+$ ★ gave a pale yellow solution. Removal of the solvent by trap-to-trap vacuum distillation, followed by recrystallization of the resulting off-white solid residue from hot toluene, afforded air-sensitive, pale yellow crystals of a 1/1 complex, $(C_6H_5)_3In \cdot W(CO)_3C_5H_5^-NBu_4^+$ (I), m.p. 165–166° (argon atm.) in 80% yield. (Anal.: Found: C, 55,54; H, 6.31; In, 12.28; N, 1.44; W, 19.61. $C_{42}H_{56}InNO_3W$ calcd.: C, 54.8; H, 6.12; In, 12.4; N, 1.52; W, 19.9%).

The IR spectrum of I in CH_2Cl_2 showed strong carbonyl stretching absorptions at 1933, 1839 and 1819 cm^{-1}(Fig.1, solid line) corresponding to the complex and weak bands at 1883 and 1764 cm^{-1} resulting from a small equilibrium amount of uncomplexed $C_5H_5(CO)_3W^-$. The shift of 40–70 cm^{-1} to higher frequencies in the complex, relative to uncomplexed anion, reflects a transfer of charge from tungsten to indium and is similar to that observed for $Cd[W(CO)_3C_5H_5]_3^-$ (ν(CO): 1922, 1844, 1831 cm^{-1})[1]. Three terminal CO stretching bands are expected on the basis of local symmetry for a $C_5H_5(CO)_3W$–X model incorporating a metal–metal bond between tungsten and indium (Fig.2A).

The use of triphenylaluminum[3] in place of triphenylindium under similar reaction conditions also led to a 1/1 complex, $(C_6H_5)_3Al \cdot W(CO)_3C_5H_5^-N(n\text{-}Bu)_4^+$ (II), in the form of air-sensitive, bright yellow crystals, (81% yield) m.p. 138–139° (argon atm.). (Anal.: Found: C, 58.77; H, 7.06; Al, 3.45; N, 1.67; W, 22.62. $C_{42}H_{56}AlNO_3W$ calcd.: C, 60.6; H, 6.65; Al, 3.24; N, 1.68; W, 22.1%).

★This salt, m.p. 115.5–116.5 (sealed, argon-filled tube), was synthesized from $C_5H_5(CO)_3W^-Na^+$ and $(n\text{-}Bu)_4N^+Br^-$ in THF and crystallized by addition of toluene.

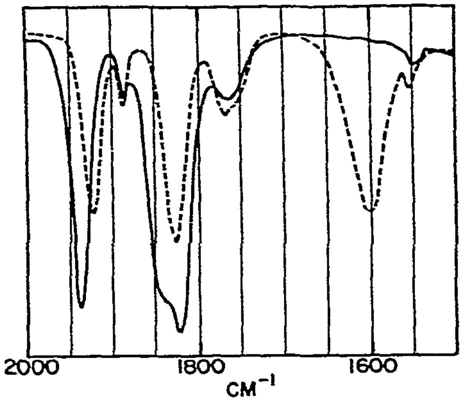
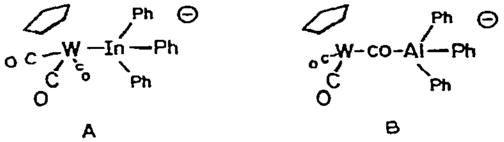


Fig.1. Infrared spectra in CH_2Cl_2 (note solvent band at 1550 cm^{-1}): solid line, $Ph_3In \cdot W(CO)_3C_5H_5^- N(n\text{-}Bu)_4^+$; dashed line, $Ph_3Al \cdot W(CO)_3C_5H_5^- N(n\text{-}Bu)_4^+$.



A B

Fig.2. Proposed structures of complex anions.

The IR spectrum of II, in contrast to that of I, showed only two strong bands in the terminal carbonyl region (1922 and 1825 cm^{-1}) but exhibited a third strong band at 1600 cm^{-1} (Fig.1, dashed line). We attribute this low frequency band to a "terminal" carbonyl group coordinated to the aluminum via the oxygen atom (Fig.2B), a situation similar to that suggested for $Ph_3PC_5H_4Mo(CO)_3 \cdot AlMe_3$[4] but differing from the well-established complex, $[C_5H_5Fe(CO)_2]_2 \cdot 2AlEt_3$ which is known to employ bridging carbonyls as sites of Lewis basicity[5]. Complex II has the lowest frequency yet reported for an O-bonded carbonyl group, presumably due to the presence of the negative charge. The two bands observed at higher wavenumbers are consistent with the presence of two terminal carbonyls on a tungsten atom having substantially less negative charge than that in the free anion. Further evidence that the $C_5H_5W(CO)_3$ moiety remains intact in this complex comes from the observation that 95% of the expected $C_5H_5W(CO)_3^- N(n\text{-}Bu)_4^+$ was recovered upon treatment of II with a small excess of pyridine in hot toluene.

The tendency of organoaluminum compounds to coordinate carbonyl oxygen is presumably a result of the inherent strength of aluminum–oxygen bonds and the assumed weakness of aluminum–tungsten bonds. On the other hand, indium-to-transition metal bonds are well established[6] and it is therefore not surprising that this feature predominates in the indium complex; similar behavior has been noted for the weak complex between diphenylcadmium and $W(CO)_3C_5H_5^-$. We are currently extending this study to a variety of organometallic–metal carbonyl systems.

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