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PRELIMINARY COMMUNICATION

A NEW ROUTE TO π-ALLYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN*

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Until relatively recently, the study of π-allyl complexes of the Group VI metals was hampered by the comparative lack of suitable syntheses. Recent advances[1-3] have improved this situation and we now wish to report the convenient and efficient synthesis of two series of π-allyl complexes of molybdenum and tungsten. One of these series is new [$(CH_3CN)_2MX$(π-allyl)$(CO)_2$] (M = Mo, W; X = Cl, Br; allyl = C_3H_5, C_4H_7, C_3H_4Cl, C_6H_9, C_3Ph_3), while the other, [C_5H_5M(π-allyl)$(CO)_2$], is known[4] but is now accessible by a greatly improved route.

The new series of π-allyl complexes is obtained by the oxidative addition of allylic halides to [$(CH_3CN)_3M(CO)_3$] (M = Mo, W)[5]. Reaction occurs rapidly with evolution of carbon monoxide and partial displacement of acetonitrile to give [$(CH_3CN)_2MX$(π-allyl)-$(CO)_2$]. The reaction has been carried out with a variety of allylic halides as indicated above and high yields, often quantitative, are readily obtained. Similar attempts to prepare π-allyl complexes of chromium from [$(CH_3CN)_3Cr(CO)_3$][5] have so far yielded only chromous halides and no evidence for even transient π-allyl complex formation has been found.

An analogous series of complexes may also be obtained by treating [$Py_3M(CO)_3$] (M = Mo, W)[6] with allyl halides, but this synthesis is less satisfactory owing to the competing quaternization reaction which predominates in the case of the more reactive halides. Both the acetonitrile and pyridine substituted π-allyl complexes of molybdenum and tungsten have been shown to have structures similar to that of [Py_2MoCl(π-C_4H_7)$(CO)_2$][2a] by spectroscopic means. These and other studies relating to the structure of the complexes will be reported at a later date. The acetonitrile complexes are of particular interest since they may be prepared in one step from molybdenum (but not tungsten) hexacarbonyl and allylic halides using acetonitrile as solvent. In addition, acetonitrile is readily replaced from [$(CH_3CN)_2MX$(π-allyl)$(CO)_2$] (M = Mo, W) bu chelate ligands or cyclopentadienyl anion and the following derivatives have been identified: [Dipy MX (π-allyl)$(CO)_2$], [Phenan MX-(π-allyl)$(CO)_2$], [$(Ph_2PC_2H_4PPh_2)MX$(π-allyl)$(CO)_2$] and [C_5H_5M(π-allyl)$(CO)_2$]. The dipyridyl and phenanthroline complexes are apparently identical with those recently reported[2b,3] while the cyclopentadienyl complexes are also already known[4]. The two-

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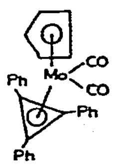
*All the new complexes reported in this paper have yielded satisfactory analytical data.

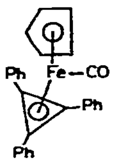
step synthesis (*vide infra*) of $[C_5H_5Mo(\pi\text{-}C_3H_5)(CO)_2]$ is probably the most convenient and efficient of this complex yet devised and has been applied to other complexes of this type.

Spectroscopic studies of $[\pi\text{-}C_5H_5Mo(\pi\text{-}C_3H_5)(CO)_2]$ have recently been reported and interpreted in terms of isomerism involving rotation of the π-allyl ligand about the metal–ligand axis. We have previously carried out similar low temperature NMR studies of this complex and our independent studies and conclusions agree with those of Davison and Rode[7] in some detail. We consider that the positional isomerism suggested by King[8] to account for the infrared spectra is not consistent with all the currently available spectroscopic data. Further details of this aspect of the current work will be published subsequently.

As part of this investigation, we have prepared the first π-cyclopropenyl complexes of a Group VI element. π-Cyclopentadienyl(π-triphenylcyclopropenyl)dicarbonylmolybdenum(I) is a member of the series of double sandwich complexes I—III of which both the molybdenum and nickel[9] members are now known. Attempts to prepare the iron analog have so far been unsuccessful.



(I)



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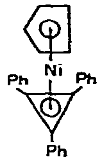

(III)

Synthesis of $[\pi\text{-}C_5H_5Mo(\pi\text{-}C_3H_5)(CO)_2]$

Molybdenum hexacarbonyl (50 g, 0.19 mole) and allyl chloride (60 ml, 0.73 mole) in acetonitrile were refluxed for 18 h to give a clear orange solution. On cooling, the solution deposited yellow crystals of pure $[(CH_3CN)_2MoCl(\pi\text{-}C_3H_5)(CO)_2]$ (53.6 g, 91%).

A tetrahydrofuran solution of $[(CH_3CN)_2MoCl(\pi\text{-}C_3H_5)(CO)_2]$ (2.7 g, 8.65 mmoles) was treated with a solution of lithium cyclopentadienide (8.65 mmoles) in tetrahydrofuran for 18 h at room temperature. After removal of solvent, the residual solid was sublimed at 60° and 10^{-3} mm to give $[\pi\text{-}C_5H_5Mo(\pi\text{-}C_3H_5)(CO)_2]$ in 72% yield.

Synthesis of $[\pi\text{-}C_5H_5Mo(\pi\text{-}C_3Ph_3)(CO)_2]$

Tris(acetonitrile)tricarbonylmolybdenum[5] (1.95 g, 6.44 mmoles) and triphenylcyclopropenylchloride[10] (1.95 g, 6.44 mmoles) were dissolved in acetonitrile (50 ml) and warmed to 70°. Gas evolution then occurred and a dark red solution was obtained. When gas evolution was complete, the solution was filtered and cooled to give pale yellow needles of pure $[(CH_3CN)_2MoCl(\pi\text{-}C_3Ph_3)(CO)_2]$ (1.0 g, 30%). This compound was converted into $[\pi\text{-}C_5H_5Mo(\pi\text{-}C_3Ph_3)(CO)_2]$ by treatment with lithium cyclopentadienide as described above. The desired complex was obtained in 10% yield as orange crystals by crystallization from hexane solution. The NMR spectrum of $[\pi\text{-}C_5H_5Mo(\pi\text{-}C_3Ph_3)(CO)_2]$ in carbon disulfide showed a singlet at $\delta = 4.84$ ppm (C_5H_5) and a complex multiplet centered at $\delta = 7.2$ ppm (C_6H_5) with intensities in the ratio 5:17.

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