

Preliminary communication

SYNTHESIS OF COORDINATIVELY UNSATURATED DIOLEFIN COMPLEXES OF TUNGSTEN(II)

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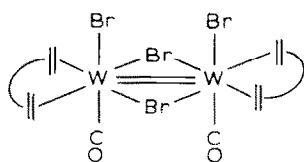
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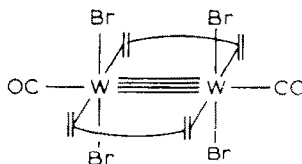
Summary

$[\text{WBr}_2(\text{CO})_4]$ reacts with cycloocta-1,5-diene, cyclooctatetraene and norbornadiene (LL) to give complexes $[\text{WBr}_2(\text{CO})\text{LL}]_2$ (I) which react with Lewis bases (L) $\{\text{L} = \text{CNBu}^t, \text{PMe}_2\text{Ph}, (\text{POMe})_3\}$ to give coordinatively unsaturated diene complexes $[\text{WBr}_2\text{CO}(\text{LL})\text{L}]$ (II) and coordinatively saturated derivatives $[\text{WBr}_2(\text{CO})(\text{LL})\text{L}_2]$ (III) (LL = NBD) and $[\text{WBr}_2(\text{CO})_2\text{L}_3]$ (IV). Two isomeric forms of the diene complexes II exist which have been separated in the case of $[\text{WBr}_2(\text{CO})(\text{NBD})(\text{PMe}_2\text{Ph})]$.

A notable feature of the chemistry of divalent molybdenum and tungsten is the ability of inorganic π -donor ligands (Cl, Br, I, O, S) [1] or four-electron π -donor alkyne ligands [2] to stabilise coordinative unsaturation at the metal centre. The intermediacy of coordinatively unsaturated complexes in organometallic and catalytic reactions is widely accepted, and following our studies of the novel chemistry of formally 16-electron alkyne complexes [2a] we now report the synthesis of coordinatively unsaturated olefin complexes.



(Ia)

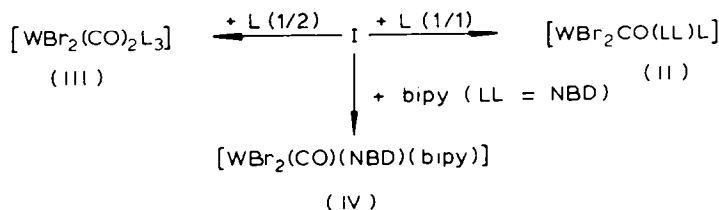


(Ib)

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Reactions of $[\text{WBr}_2(\text{CO})_4]$ with diene LL (LL = cyclooctatetraene, COT, 1,5-cyclooctadiene, COD, or norbornadiene, NBD) gives black crystalline adducts $[\text{WBr}_2(\text{CO})\text{LL}]_n$ (I)*. Molecular weight studies, although not entirely conclusive due to sample instability, suggest a dinuclear structure ($n = 2$) in solution, a conclusion supported by the presence of two $\nu(\text{CO})$ modes in the IR spectra and a molecular ion $P^+ = 926$ a.m.u. in the mass spectra of I (LL = NBD). Interestingly, however, mononuclear ions $P/2$, $P/2 - \text{CO}$ and $P/2 - (\text{CO} + \text{Br})$ are significantly more intense, while dinuclear ions are not observed with LL = COT or COD. Spectroscopic data $[\text{WBr}_2(\text{CO})(\text{NBD})]_2$: IR (CH_2Cl_2): $\nu(\text{CO})$ 2070w, 2000vs cm^{-1} ; ^1H NMR: δ (ppm) 4.42 (t, 4H), 3.98 (bm, 2H), 0.79 (t, 2H); mass spectrum: $P^+ = 926$ and ions $P - 2\text{CO}$, $P - (\text{CO} + \text{Br})$, $P - (2\text{CO} + \text{Br})$, $P/2 = 462$, $P/2 - (\text{CO})$, $P/2 - (\text{C}_7\text{H}_8)$, $P/2 - (\text{CO} + \text{Br})$. Structure Ia is proposed for these derivatives despite the simplicity of the ^1H NMR spectra, which is probably deceptive (vide infra). An alternative structure (Ib) cannot be excluded, but the low stability of $\text{W}\equiv\text{W}^{4+}$ units [3], coupled with the fact that π -acceptor ligands such as CO destabilise quadruply bonded $\text{M}\equiv\text{M}$ dimers [4], makes this less likely.

Cleavage of the dimeric unit can be achieved chemically by Lewis bases, which give various product types depending on the reaction conditions and the reactants (see Scheme 1). Use of 1/1, ligand to metal ratios gives coordinatively un-

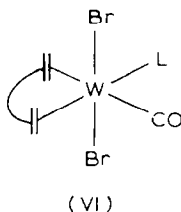
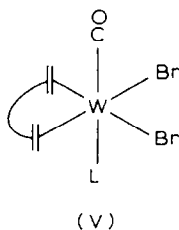


SCHEME 1

saturated diene complexes (II) in most cases, although dicarbonyls (III, L = CNBu^t , PMe_2Ph) are also obtained in low yield from I (LL = COT or COD). Complexes of type III are obtained preferentially from I (LL = COT or COD) when 2/1 ligand to metal molar ratios are employed. Related complexes $[\text{MX}_2(\text{CO})_3\text{L}_2]$ have been isolated previously from reactions of $[\text{MX}_2(\text{CO})_4]$ (M = Mo, W; X = halide) with Lewis bases [1a,5]. Interestingly, norbornadiene is not readily displaced under these conditions, and 1/1 adducts $[\text{WBr}_2(\text{CO})(\text{NBD})\text{L}]$ (II, L = CNBu^t , py, PMe_2Ph , $\text{P}(\text{OMe})_3$) or 1/2 adducts $[\text{WBr}_2\text{CO}(\text{NBD})\text{L}_2]$ (IV, $\text{L}_2 = 2,2'$ -bipyridyl), are obtained. This may reflect the greater thermodynamic stability of norbornadiene complexes resulting from coordination of strained double bonds.

Complexes II can obviously exist in several isomeric forms, and although one isomer was isolated in most cases, ^1H and ^{31}P NMR studies indicated that isomerisation occurs in solution. In the case of $[\text{WBr}_2(\text{CO})(\text{NBD})(\text{PMe}_2\text{Ph})]$ two distinct isomers were isolated. Spectroscopic data. IIa: orange crystals, IR (CHCl_3): $\nu(\text{CO})$ 1953s cm^{-1} ; ^1H NMR: δ (ppm) 7.60 (m, 2H, Ph), 7.40 (m, 3H, Ph), 4.06 (t, 4H), 3.63 (bs, 2H), 2.24 (d, 6H, Me), 1.42 (bs, 2H); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ (ppm) -28.62(s) (δ (H_3PO_4) 0). IIb: dark green crystals, IR (CHCl_3): $\nu(\text{CO})$ 1974s cm^{-1} ; ^1H NMR: δ (ppm) 7.94 (m, 2H, Ph) 7.48 (m, 3H, Ph), 4.69 (bm, 2H), 3.87 (bm, 1H), 3.46

*Satisfactory analytical data were obtained for all complexes.



(bm, 1H), 3.22 (bm, 2H), 2.15 (d, 6H, Me), 0.43 (bs, 2H); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ (ppm) -14.67 (s). The ^1H NMR spectrum of IIa exhibits only three norbornadiene proton signals (cf. I), similar to those of the free diene but with a coordination shift of the olefinic protons resonance to higher field. Since the highest symmetry isomers of II can only possess a single plane of symmetry the ^1H NMR spectrum is deceptively simple, a comment which may also apply to the parent dimer I. A lower symmetry is implied by the greater number of peaks in the ^1H NMR of IIb but the absence of diastereotopic PMe_2Ph methyl groups revealed by the presence of only one methyl group doublet indicates that a plane of symmetry is still present. Accordingly the two isomeric structures must be V and VI. Based on ^1H NMR data $[\text{WBr}_2(\text{CO})(\text{NBD})(\text{CNBu}^t)]$ has a similar structure to IIa while $[\text{WBr}_2(\text{CO})(\text{NBD})\text{L}]$ ($\text{L} = \text{pyridine}$ or $\text{P}(\text{OMe})_3$) are similar to IIb. Only one isomer of II ($\text{LL} = \text{COT}$ or COD) was observed in all cases except $[\text{WBr}_2(\text{CO})-(\text{COT})\text{P}(\text{OMe})_3]$, for which two forms were detected in solution by ^1H NMR spectroscopy.

It is informative to compare the stoichiometry of complexes II with that of known zero-valent molybdenum and tungsten complexes $[\text{M}(\text{CO})_4(\text{diene})]$ (diene = norbornadiene or 1,5-cyclooctadiene [6]) since the eighteen-electron configuration of the latter contrasts with the sixteen electron configuration of the former. We attribute this to the presence in II of bromo ligands, which in principle are capable of acting as π -donors and therefore stabilising coordinative unsaturation at the metal centre. It may be that coordinatively unsaturated complexes of this type can serve as models for intermediates in e.g. olefin metathesis and polymerisation reactions which involve molybdenum and tungsten halide catalysts. We are currently investigating the chemical and catalytic properties of the complexes with this possibility in mind.

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