Nucleophilic Addition of Hydrazines at Bridging Isocyanate to give Urea-type Ligands

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The clusters $[Os_3(CO)_{12-x}(MeCN)_x]$ (x = 0, 1, or 2) react with hydrazine or 1,1′-dimethylhydrazine to give the compounds $[Os_3H(CO)_{10}(NHCONHNR_2)]$ (R = H or Me) which have also been formed by addition of NH_2NR_2 to $[Os_3H(NCO)(CO)_{10}]$, itself formed from HNCO and $[Os_3(CO)_{10}(MeCN)_2]$.

The chemistry of metal carbonyls in liquid ammonia has been reviewed recently;[1] attack by ammonia may be at the metal atoms or at CO. If a carbonyl complex has readily replaceable ligands, ammonia compounds may be obtained as for $[Os_3(CO)_{11}(NH_3)]$, the product of treating $[Os_3(CO)_{11}(MeCN)]$ with ammonia.[2] Alternatively, if a compound readily forms adducts with nucleophiles, then ammonia may add directly at the metal atom; the purple solution of $[Os_3H_2(CO)_{10}]$ readily forms adducts[3] and in cyclohexane immediately becomes yellow on addition of ammonia yielding yellow crystals of $[Os_3H_2(CO)_{10}(NH_3)]$ (**1**) quantitatively.† Redissolving these crystals in cyclohexane and warming to 40 °C regenerates the parent dihydride compound. In general, however, ammonia and amines attack CO of co-ordinatively saturated metal carbonyl compounds. For example, $[Os_3(CO)_{12}]$ reacts with amines, RNH_2, at or below room temperature to give the complexes $[Os_3H(CO)_{10}(RNHCO)]$ (**2**) by direct addition at CO.[4] $[Os_3(CO)_{12}]$ readily dissolves in liquid ammonia at room temperature to give what we believe to be $[Os_3H(CO)_{10}(NH_2CO)]$ [on the basis of a similar ν(CO) spectrum to those of compounds (**2**)] but because of lack of solubility and decomposition on chromatography (SiO_2) this compound has not been properly purified or characterised.

We set out to synthesise the compound $[Os_3(CO)_{10}(N_2H_4)]$ containing bridging hydrazine which we then hoped to oxidise to bridging N_2H_2 or N_2. The complex $[Os_3(CO)_{10}(MeCN)_2]$ might have given this compound directly with hydrazine but instead gave a mixture on reaction with neat hydrazine or with a small excess of hydrazine in dichloromethane. Similar mixtures were also obtained from $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{12}]$, from which we were only able to isolate compound (**3a**) (5—10%) which analysed as $[Os_3(CO)_{11}(N_3H_5)]$ and gave the highest mass ion (*m/e* 931

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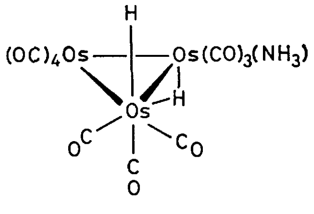
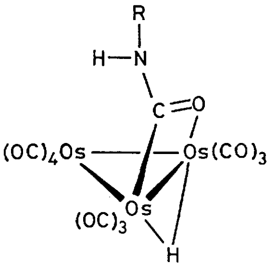
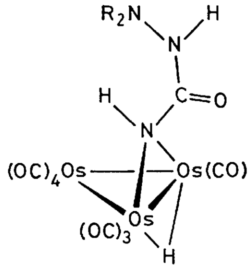
† Spectral data for (**1**): ν(CO) (cyclohexane) 2102w, 2062s, 2049s, 2024s, 2004m, 1999m, 1987s, 1982sh, and 1971w cm^{-1}. (**3a**): ν(CO) (cyclohexane) 2107w, 2071w, 2056s, 2020s, 2007s, 2001s, 1983w, and (KBr) 1695s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ −14.64 (d, OsH), 7.25 (br s, NH), 6.84 (s, NH), and 3.93 (s, NH_2). (**3b**): ν(CO) (cyclohexane) 2108w, 2072s, 2058s, 2021s, 2008sh, 2001s, 1984w, and (KBr) 1700 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ −14.67 (d, OsH), 2.58 (s, Me_2), 6.32 (s, NH), and 7.32 (br s, NH). (**4**): ν(CO) (cyclohexane) 2226s (NCO), 2112w, 2077s, 2065m, 2027s, 2022sh, 2012m, and 1990w cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ −13.82 (s). Compounds (**3**) and (**4**) gave parent molecular ions in their mass spectra.



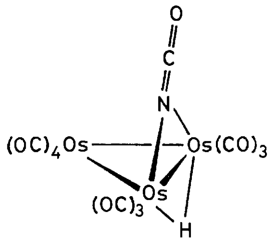
(1)



(2)



(3) a; R = H
b; R = Me



(4)

based on ^{192}Os) corresponding to this in its mass spectrum. The analogous compound $[Os_3(CO)_{11}(N_3H_3Me_2)]$ (**3b**) was obtained similarly from Me_2NNH_2. Spectroscopically† (**3a**) and (**3b**) were identified as hydrido-complexes of type $[Os_3H(CO)_{10}(NHX)]$ by comparison with other compounds of this type,[5] in particular there was a hydride ^1H n.m.r. doublet at δ *ca.* −15. Group X apparently contains a carbonyl group [ν(CO) *ca.* 1700 cm^{-1}]. *X*-Ray crystal structure analyses of both (**3a**) and (**3b**) have clearly established the structures shown.[6]

Presumably the formation of the urea-derivatives (**3a**) and (**3b**) requires nucleophilic attack by hydrazine at a CO ligand as in the $[Os_3(CO)_{12}]$-catalysed conversion of benzylamine to dibenzylurea.[4a] A minor product from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with hydrazine gave a molecular ion [*m/e* 899 based on ^{192}Os] in its mass spectrum. This corresponded to the isocyanate $[Os_3H(CO)_{10}(NCO)]$ (**4**), so we prepared this compound. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with KNCO in acidic aqueous methanol at room temperature gave only $[Os_3H(CO)_{10}(OH)]$ (80%), but a room temperature treatment of the bis(acetonitrile) compound in CH_2Cl_2 with an excess of dry HNCO (prepared by decomposing cyanuric acid at 700 °C[7]) gave (**4**) (87%).† Compound (**4**) is unstable towards t.l.c. (SiO_2) being susceptible to nucleophilic addition. Indeed hydrazine and *N,N'*-dimethylhydrazine react readily and almost completely with (**4**) in CH_2Cl_2 at room temperature to give (**3a**) and (**3b**) respectively. Organic isocyanates, RNCO, react in this way with hydrazine to give $RNHCONHNH_2$,[8] but to our knowledge such a reaction has not been reported for a transition metal isocyanate. Compound (**4**) reacts generally with HX (X = OR or NR_2) to give the compounds $[Os_3H(CO)_{10}(NHCOX)]$ which relate directly with (**3**).

If (**4**) is an intermediate in the formation of (**3**) from $[Os_3(CO)_{12}]$ and hydrazines, the problem of its formation remains. Perhaps compounds of type (**2**) (R = NH_2 or NMe_2) eliminate NH_3 or Me_2NH to give the isocyanate, but we have not confirmed this.

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References

1 H. Behrens, *Adv. Organomet. Chem.*, 1980, **18**, 1.
2 G. Suss-Fink, *Z. Naturforsch., Teil B*, 1980, **35**, 454.
3 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1975, **88**, C21; *Ibid.*, 1976, **114**, 313; J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, 1975, **97**, 4145.
4 (a) K. A. Azam, C. Choo Yin, and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1978, 1201; (b) A. J. Arce and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1980, 1102; (c) R. Szostak, C. E. Strouse, and H. Kaesz, *J. Organomet. Chem.*, 1980, **191**, 243; (d) Y. C. Lin, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1981, **103**, 1216.
5 C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1974, 1013; E. G. Bryan, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 1328.
6 M. B. Hursthouse, J. D. J. Backer-Dirks, and N. Walker, unpublished results.
7 N. Groving and A. Holm, *Acta Chem. Scand.*, 1965, **19**, 1768.
8 L. F. Andrieth and B. A. Ogg, 'The Chemistry of Hydrazine,' Wiley, New York, 1951, pp. 213—218; M. N. Hughes, 'The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives,' ed. A. A. Newman, Academic Press, New York, 1975, pp. 51—54.