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Preliminary communication

TRIRUTHENIUM CLUSTERS CONTAINING DIMETHYLAMINO-SUBSTITUTED ALLYL AND ALLENYL LIGANDS: THE TRANSMISSION OF ELECTRONIC SUBSTITUENT EFFECTS THROUGH CLUSTERS

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Summary

The NMe_2 substituent in $CH_3C{\equiv}CCH_2NMe_2$ facilitates oxidative addition to $Ru_3(CO)_{12}$ to give the isomeric allenyl cluster $HRu_3(CO)_9(MeC{=}C{=}CHNMe_2)$ and allylic cluster $HRu_3(CO)_9(MeCCHCNMe_2)$. The barrier to rotation about the internal ligand C—NMe_2 bond is sensitive to the nature of L in $HRu_3(CO)_8L$-$(MeCCHCNMe_2)$, even though L is remote from this bond, and also to protonation of the cluster. Lower barriers are associated with increased electron-availability on the cluster.

The oxidative addition of non-terminal alkynes (L) to $Ru_3(CO)_{12}$ gives two isomeric compounds of general formula $HRu_3(CO)_9(L\text{-}H)$. The kinetically favoured isomer contains a 1-η^1-1,2-η^2-allenyl ligand which isomerises by hydrogen atom migration to the more stable di-η^1-η^3-allyl isomer [1]. We are currently examining the reactions of metal carbonyl clusters with functionalised alkynes to see how the function modifies the reaction pathways and to generate novel clusters.

The reaction between $Ru_3(CO)_{12}$ and $CH_3C{\equiv}CCH_2NMe_2$ occurred readily in refluxing cyclohexane and after 1 h two isomeric products were isolated, cluster **1** (50%) and cluster **2** (40%); these were characterised by ^1H NMR, IR and mass spectra. Clusters **1** and **2** are of the usual type obtained from simple non-terminal alkynes, but the Me_2N group causes a marked acceleration of their rates of formation and a marked increase in yield. As in other cases,

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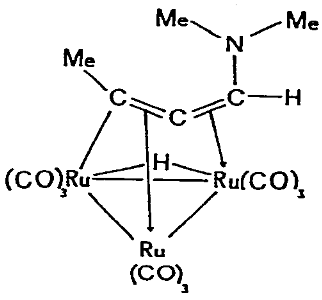
TABLE 1

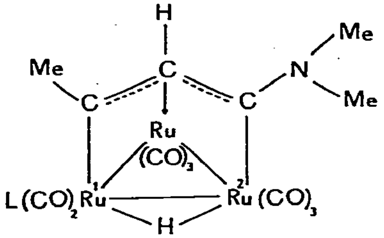
PHYSICAL DATA FOR THE COMPOUNDS PREPARED

Compound	ν(CO) (cm^{-1})[a]	^{1}H NMR (δ, ppm)[b]				T_c (°C)[c]	Rotational energy barrier (kJ mol^{-1})[d]
		NMe$_2$	C—Me	C—H	Ru—H		
1	2083m, 2053s, 2030vs, 2013m, 2000m, 1988w	3.30(s) 2.95(s)	2.52(s)	7.31(s)	−18.83(s)	0	57.7
2	2089m, 2060s, 2034vs, 2018m, 2004m, 1996m, 1974w	3.55(s) 3.30(s)	2.72(s)	6.00(d) (*J*(HH) 4.0)	−17.58(d) (*J*(HH) 4.0)	25	64.4
3a	2075s, 2038vs, 2022s, 1999m, 1989m	3.31(s) 2.95(s)	2.60(d) (*J*(PH) 7.0)	5.43(d) (*J*(HH) 3.0)	−18.00(dd) (*J*(HH) 3.0, *J*(PH) 18.0)	14	61.1
3b	2069s, 2029vs, 2012s, 1996w, 1987ms, 1970m	3.49(s) 3.28(s)	2.14(d) (*J*(PH) 4.0)	5.86(d) (*J*(HH) 3.0)	−17.67(dd) (*J*(HH) 3.0, *J*(PH) 19.0)	−10	56.9
3c	2070s, 2030vs, 2010vs, 1984s, 1964m, 1947w	3.48(s) 3.24(s)	2.61(d) (*J*(PH) 3.0)	5.90(d) (*J*(HH) 3.0)	−17.97 (*J*(HH) 3.0, *J*(PH) 16.0)	−15	55.6
4	2103s, 2074vs, 2060s, 2035s, 2020m	3.58(s) 3.47(s)	2.55(d) (*J*(PH) 2.0)	6.33(d) (*J*(HH) 3.0)	−15.15(dd) (*J*(HH) 1.5, *J*(PH) 17.5) −18.75(ddd) (*J*(HH) 1.5, 3.0, *J*(PH) 17.5)	>>25	

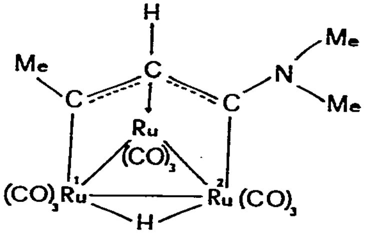
[a] 1, 2, 3a, 3b and 3c measured in n-hexane; 4 measured in $CHCl_3/CF_3COOH$ solution. [b] Measured in $CDCl_3$; *J* in Hz. [c] T_c for coalescence of NMe$_2$ singlets (± 1°C). [d] Estimated from T_c, $\Delta\nu$ and Eyring equation.



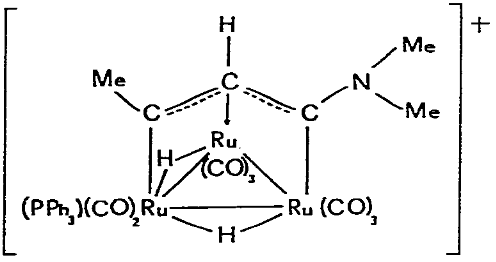
(1)



(3a) L = P(OPh)$_3$
(3b) L = P Ph$_3$
(3c) L = P Pr$^i_3$



(2)



(4)

compound 1 is converted into 2 almost quantitatively in refluxing n-heptane (1 h) [2].

Since each compound shows two separate ^{1}H NMR singlets for the NMe$_2$ group at low temperatures, the C—NMe$_2$ bond must have some multiple-bond character [3]. These singlets coalesce on warming; the coalescence temperatures (T_c) are 0°C for 1 and 25°C for 2. The other ^{1}H NMR signals are temperature-independent. We considered the possibility that the rotational energy barrier for the C—NMe$_2$ bond might be a sensitive measure of variations in electron density at the metal cluster since the barrier should increase with increasing electron-withdrawal by the cluster. This could then provide a simple, directly accessible parameter as an alternative to the spectral parameters (IR and NMR) commonly used. We have chemically modified compound 2 to test this idea.

Group V donor ligands (PPr$^i_3$, PPh$_3$, and P(OPh)$_3$) react with 2 (mole ratio 2:1) in refluxing cyclohexane (1 h) to give only one product, compound 3, in each case. ^{1}H NMR spectra indicate that a CO ligand on Ru(1) is replaced rather than one on the corresponding atom Ru(2). Possibly the observed π-donation from NMe$_2$ deactivates the CO ligands on Ru(2) towards substitution, and certainly those on Ru(1) are significantly more labile [4].

The ^{1}H NMR spectra of compounds 3 are quite similar to that of 2 except for ^{31}P-coupling and for lower temperatures for coalescence of the NMe$_2$ singlets (see Table 1). The rotational barriers are in the order 2 > 3a > 3b > 3c; that is, the barriers decrease with increasing σ-donor or decreasing π-

acceptor abilities of the ligands at Ru(2). The simplest explanation is that the more electron-rich cluster allows less donation from the NMe_2 group and less multiple bonding in the C—NMe_2 bond, but it is interesting that this bond is sensitive to substitution at a remote part of the cluster. It would be of interest to know whether the effect is transmitted through the π-system of the allyl ligand or through the metal—metal bond.

The same effect shows up when a few drops of CF_3CO_2H are added to a chloroform solution of 3b; this gives the dihydrido cation 4 in solution, for which two NMe_2 singlets are observed at room temperature. The coalescence temperature and rotational barrier are significantly raised, consistent with an increased π-donation from the NMe_2 group. It is noteworthy also, that the metal atoms are more basic than the nitrogen atom.

These results show how a specific property of a functional group, in this case an internal ligand rotation, may be used to assess electronic demands of the metal atoms and to evaluate cooperative effects within clusters.

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