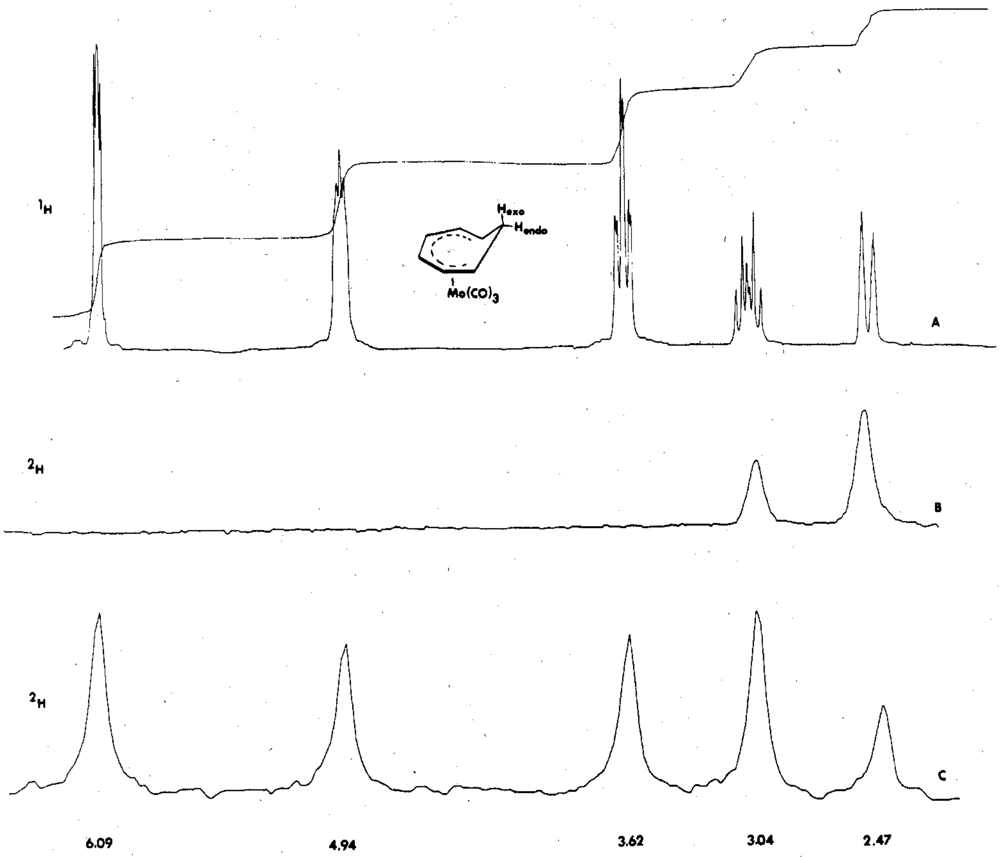

Figure 2. (A) A 270-MHz ^1H spectrum of $C_7H_8Mo(CO)_3$ in deuteriochloroform. (B) A 41.4-MHz $^2H\{^1H\}$ spectrum of $C_7H_7DMo(CO)_3$ in chloroform. This sample was prepared by treatment of $[C_7H_7Mo(CO)_3]PF_6$ with $NaBD_3CN$. (C) The ^2H spectrum of $C_7H_7DMo(CO)_3$ after being heated in octane for 1 h.

shown that a similar rearrangement apparently occurs in $C_6D_6HMn(CO)_3$ via an η^4-benzene intermediate.[26] This nonspecific migration contrasts with the interpretation of Pauson[27] of [1,5]-migrations in seven-membered rings attached to $Cu(CO)_3$. As Lamanna and Brookhart[26] suggest, however, the apparent specificity of the rearrangment probably arises from preferred geometries of the substituted intermediates.

The current interest in these metal-assisted rearrangments[2,26,27] suggests that many workers may be using a variety of physical methods to identify the isomers. It is clear from our work that NMR, particularly ^2H NMR, is the most reliable technique for following specificity and that low-frequency IR bands may be suspect.[28] A further caveat regarding intensity measurements in ^1H NMR is in order. We have found that the relaxation times of the endo and exo protons are significantly different and those in a CHD group are particularly long. Thus, the use of pulsed NMR spectrometers can often lead to erroneous measurements of relative intensities of H_{olefin} to H_{endo} to H_{exo}, if relaxation reagents or long pulse delays are not used.

Although we have considered only nucleophilic hydride addition, one might also note that protonations appear to occur by initial addition to the metal followed by migration to an endo position on the ring.[17,29,30]

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Registry No. $C_7H_8Mo(CO)_3$, 12125-77-8; $C_7H_7DMo(CO)_3$, 74244-62-5; $[C_7H_7Mo(CO)_3]PF_6$, 56253-18-0.

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(28) The coupling of the vicinal H to the endo and exo methylene H(D) appears to provide the most reliable method of assignment. The upfield shift of H_{exo}, found in the $C_7H_8M(CO)_3$ complexes and attributed to ring currents,[29] may be reversed in some cases. That is, H_{endo} is at higher field in some rhodium complexes.[17,30]

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A Comment on the Nature of "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$"

Sir:

Otsuka and co-workers have recently reported the preparation of compounds formulated as "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$"[1] (R = Me or Et) by the reaction of $[MoO_2(S_2CNR_2)_2]$ with $PhNHNH_2$. As we have also studied this reaction and appeared to have isolated quite different prod-

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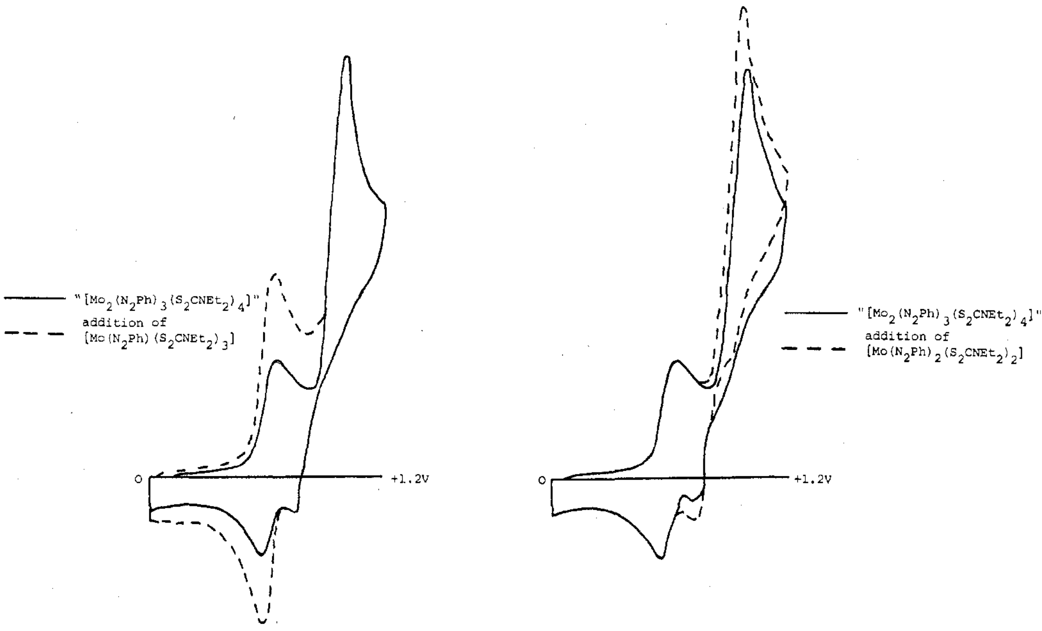

Figure 1. Cyclic voltammograms of "$[Mo_2(N_2Ph)_3(S_2CNMe_2)_4]$".

Table I. Cyclic Voltammetry Data

	sample[a]	$^1E_{1/2}^{ox}$ [b,c]/ V	$^2E_p^{ox}$/ V	ratio[d] $^1i_p/^2i_p$
1	$[Mo(N_2Ph)(S_2CNEt_2)_3]$	+0.640		
2	$[Mo(N_2Ph)_2(S_2CNEt_2)_2]$		+1.021	
3	"$[Mo_2(N_2Ph)_3(S_2CNEt_2)_4]$"	+0.644	+1.020	0.370
4	"$[Mo_2(N_2Ph)_3(S_2CNEt_2)_4]$"	+0.638	+0.990	0.358
5	$[Mo(N_2Ph)(S_2CNMe_2)_3]$	+0.638		
6	$[Mo(N_2Ph)_2(S_2CNMe_2)_2]$		+1.038	
7	"$[Mo_2(N_2Ph)_3(S_2CNMe_2)_4]$"	+0.635	+1.034	0.358

[a] Sample 3 was supplied by Professor Otsuka. Samples 4 and 7 were prepared according to Otsuka et al.[1] [b] All measurements were made in dimethylformamide. [c] All potentials were quoted vs. saturated calomel electrode. [d] i_p = cyclic voltammetric peak current.

ucts,[2,3] we decided to make a comparison of Otsuka's product with ours. The results of this study show unequivocally that "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$" is, in fact, a mixture of $[Mo(N_2Ph)(S_2CNR_2)_3]$ and $[Mo(N_2Ph)_2(S_2CNR_2)_2]$.

The samples of "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$" were either supplied kindly by Professor Otsuka or prepared by using the method reported by Otsuka et al.[1] ^1H NMR and microanalytical data for samples from both sources were in close agreement. The cyclic voltammograms (Figure 1) showed a reversible oxidation and an irreversible oxidation at the same potentials as those observed in the complexes $[Mo(N_2Ph)(S_2CNR_2)_3]$ and $[Mo(N_2Ph)_2(S_2CNR_2)_2]$, respectively.[2] Furthermore, in the Otsuka compounds a reversible oxidation wave developed at +0.78 V with continuous scanning, and this was also observed for $[Mo(N_2Ph)_2(S_2CNR_2)_2]$ under similar conditions.

As further conclusive evidence authentic samples of $[Mo(N_2Ph)(S_2CNMe_2)_3]$ and $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ were added to separate solutions of the Otsuka compound "$[Mo_2(N_2Ph)_3(S_2CNMe_2)_4]$". The cyclic voltammograms of these solutions showed enhancement of the peak current at the oxidation potentials observed for $[Mo(N_2Ph)(S_2CNMe_2)_3]$ and $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$, respectively (Figure 1). It has also been calculated from the cyclic voltammetric data that the product "$[Mo_2(N_2Ph)_3(S_2CNMe_2)_4]$" contains approximately 30% $[Mo(N_2Ph)(S_2CNMe_2)_3]$. The ^1H NMR, although complicated in the (dithiocarbamato)alkyl region, is consistent with the Otsuka product being a mixture.

The diffuse reflectance spectrum of the compound "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$" shows absorbance maxima at wavelengths of 24 390 cm and 17 985 cm^{-1}, the same as those observed for the complexes $[Mo(N_2Ph)(S_2CNR_2)_3]$ and $[Mo(N_2Ph)_2(S_2CNR_2)_2]$, respectively. Furthermore, the infrared spectrum of the Otsuka product as a Nujol mull is a superposition of the spectra of $[Mo(N_2Ph)(S_2CNR_2)_3]$ and $[Mo(N_2Ph)_2(S_2CNR_2)_2]$. This rules out the unlikely possibility that the cyclic voltammetric results are due to disproportionation of "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$" in solution.

Registry No. $Mo_2(N_2Ph)_3(S_2CNMe_2)_4$, 68813-08-1; $Mo_2(N_2Ph)_3(S_2CNEt_2)_4$, 68813-09-2; $Mo(N_2Ph)(S_2CNEt_2)_3$, 73970-86-2; $Mo(N_2Ph)_2(S_2CNEt_2)_2$, 74006-57-8; $Mo(N_2Ph)(S_2CNMe_2)_3$, 53540-27-5; $Mo(N_2Ph)_2(S_2CNMe_2)_2$, 74006-58-9.

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