

Carbonyl Halides of the Group VII Transition Metals. VI* Further Comments on Derivatives of Rhenium Halocarbonyls and Bis(diphenylarsino)methane

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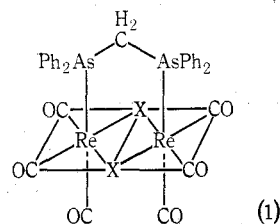
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Abstract

A revision is made of the proposed structures of a series of rhenium halocarbonyls with dam on the basis of recent crystallographic evidence and a reassessment of n.m.r. data.

Introduction

In a recent paper¹ we described a wide variety of complexes formed by reaction between rhenium halopentacarbonyls, $[\text{Re}(\text{CO})_5\text{X}]$, and bis(diphenylarsino)methane, dam. The purpose of this note is to revise ideas on the structures of two types of compound formed in this system. This revision is undertaken in the light of very recent X-ray structural evidence and a reassessment of n.m.r. data.



For the compounds $[\text{Re}_2(\text{CO})_6(\text{dam})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) six possible structures were considered, only one of which (1) contained six-coordinate rhenium and obeyed the 18-electron rule. The other structures all involved five-coordinate rhenium. Although the structure (1) was very attractive, it was rejected because 'molecular models indicate the dam ligand would have difficulty spanning the rhenium-halogen bridge, particularly in the iodo complex'.¹ In addition, at that time, we knew of no example in which dam bridged two metal atoms which were simultaneously bridged by other groups.

The first hint that we had made a faulty decision arose from an n.m.r. study of the isoelectronic $[\text{W}_2(\text{CO})_4(\text{NO})_2(\text{dam})\text{X}_2]$ series which was shown unequivocally to contain a bridging dam group as well as bridging halogens between the tungsten atoms.² The hint was confirmed by an X-ray diffraction study³ of $[\text{Re}_2(\text{CO})_6(\text{dam})\text{Cl}_2]$ which established structure (1). An interesting feature of the structure is that there is indeed strain in the dam bridge, but that this is relieved not by opening the 'bite'

* Part V, *Aust. J. Chem.*, 1976, 29, 1657.

¹ Colton, R., and Garrard, J. E., *Aust. J. Chem.*, 1973, 26, 529.

² Colton, R., and Commons, C. J., *Aust. J. Chem.*, 1973, 26, 1493.

³ Commons, C. J., and Hoskins, B. F., *Aust. J. Chem.*, 1975, 28, 1201.

of the ligand as might have been expected, but rather by a distortion of the octahedral environment about the rhenium atoms. Very recent determinations of the crystal structures of $[\text{Mn}_2(\text{CO})_5(\text{dpm})]$ ^{4,5} and $[\text{Pd}(\text{dpm})\text{Br}]_2$ ^{6,7} have established that not only one, but two dam or dpm [dpm = bis(diphenylphosphino)methane] groups may bridge two metal atoms which are either bridged by other groups or directly metal-metal bonded.

We now wish to reconsider the structure of the compounds $[\text{Re}(\text{CO})_2(\text{dam})\text{X}]$ in the light of the new knowledge that dam can bridge two metal atoms and also on a reassessment of n.m.r. data. It should be noted that these compounds are insoluble, so molecular weights are not available.

Discussion

We have previously pointed out¹ that the mode of coordination of dam (i.e. monodentate or didentate) in a series of similar compounds can be determined from the position of the methylene resonance. We also pointed out¹ that in both $[\text{Re}_2(\text{CO})_6(\text{dam})\text{X}_2]$ and $[\text{Re}(\text{CO})_2(\text{dam})\text{X}]$ the methylene resonance fell halfway between the characteristic positions for monodentate and bidentate dam on rhenium(I), and we suggested that this position represented bridging dam. This assignment has now been confirmed by the structural study on $[\text{Re}_2(\text{CO})_6(\text{dam})\text{Cl}_2]$ and consequently $[\text{Re}(\text{CO})_2(\text{dam})\text{X}]$ may also contain dam bridging between two rhenium atoms in an environment similar to that in $[\text{Re}_2(\text{CO})_6(\text{dam})\text{Cl}_2]$.

Table 1. N.m.r. data (methylene region) of dam complexes¹

χ , difference in position of methylene resonance between chloro and iodo derivatives

Compound	δ (ppm)			χ (ppm)	Comments	
	X = Cl	X = Br	X = I		Halogens	dam
$\text{Re}(\text{CO})_4(\text{dam})\text{X}$	3.16	3.24	3.43	0.27	terminal	monodentate
$\text{Re}(\text{CO})_3(\text{dam})\text{X}$	4.92	4.92 ^A	5.18 ^A	0.26	terminal	bidentate
$\text{Re}_2(\text{CO})_6(\text{dam})\text{X}_2$	3.60	3.98	4.45	0.85	bridging	bridging
$\text{Re}(\text{CO})_3(\text{dam})_2\text{X}$	2.76 ^A	2.81 ^A	2.89 ^A	0.13	terminal	monodentate
$\text{Re}(\text{CO})_2(\text{dam})\text{X}$	3.50	4.10		0.6	bridging?	bridging

^A Mid point of a multiplet.

The n.m.r. data from ref.¹ are reproduced in Table 1 and are further assessed as follows. There appears to be a relation between the variation of the methylene resonance position and the identity of the halogen, depending on whether the halogen is terminal or bridging. Thus in the series $[\text{Re}(\text{CO})_4(\text{dam})\text{X}]$, $[\text{Re}(\text{CO})_3(\text{dam})\text{X}]$, and $[\text{Re}(\text{CO})_3(\text{dam})_2\text{X}]$ the difference (χ) in position of the methylene resonance on going from chloro through bromo to iodo in each series is <0.3 . Each of these series contains terminal halogens only. We note that the value of χ is independent of whether dam is monodentate or bidentate, or whether the resonance is a singlet or an AB quartet. In $[\text{Re}_2(\text{CO})_6(\text{dam})\text{X}_2]$ which is now known to contain bridging halogens, the variation in the position of the methylene resonance between chloro and iodo

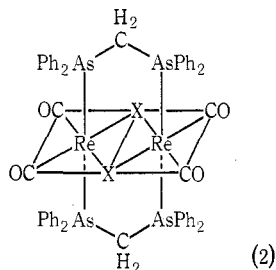
⁴ Colton, R., Commons, C. J., and Hoskins, B. F., *J. Chem. Soc., Chem. Commun.*, 1975, 363.

⁵ Commons, C. J., and Hoskins, B. F., *Aust. J. Chem.*, 1975, **28**, 1663.

⁶ Colton, R., Farthing, R. H., and McCormick, M. J., *Aust. J. Chem.*, 1973, **26**, 2607.

⁷ Holloway, R. G., Penfold, B. R., Colton, R., and McCormick, M. J., *J. Chem. Soc., Chem. Commun.*, in press.

compounds is very much greater ($\chi = 0.85$). Although we have no data for $[\text{Re}(\text{CO})_2(\text{dam})\text{I}]$ because of solubility problems, it is apparent from the difference between $[\text{Re}(\text{CO})_2(\text{dam})\text{Cl}]$ and $[\text{Re}(\text{CO})_2(\text{dam})\text{Br}]$ ($\chi = 0.6$) that there is the same wide variation in the $[\text{Re}(\text{CO})_2(\text{dam})\text{X}]$ series. The conclusion we draw from this data is that $[\text{Re}(\text{CO})_2(\text{dam})\text{X}]$ also contains halogen bridges. This result was inaccessible by far-infrared spectroscopy because of the large number of ligand bands.



As a result of these new pieces of information it is suggested that structure (2) is the most likely for $[\text{Re}(\text{CO})_2(\text{dam})\text{X}]$. This structure is consistent with the infrared spectrum (carbonyl region) of the complex¹ and it is more satisfying than the originally suggested five-coordinate structures since it gives six-coordinate rhenium(I) and obeys the 18-electron rule.

Finally, we suggest that the variation of methylene resonances with the type of halogen coordination may be a general phenomenon. Thus, we have prepared a similar series of manganese complexes with dam and they also follow these trends in the behaviour of the methylene signal.⁸ In addition, the compounds $[\text{W}(\text{CO})_3(\text{NO})(\text{dam})\text{X}]$, $[\text{W}(\text{CO})_2(\text{NO})(\text{dam})_2\text{X}]$, $[\text{W}(\text{CO})_2(\text{NO})(\text{dpm})\text{X}]$ and $[\text{W}(\text{CO})(\text{NO})(\text{dpm})_2\text{X}]$ all have terminal halogens and all have $\chi < 0.3$, but $[\text{W}(\text{CO})_2(\text{NO})\text{X}]_2(\text{dam})$ which have bridging halogens have $\chi = 0.78$.²

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⁸ Colton, R., and McCormick, M. J., *Aust. J. Chem.*, 1976, **29**, 1657.