Isonitrile ligand effects on small-molecule-sequestering in bimetalladodecaborane clusters[☆]

Jonathan Bould [a,b,c,]*, Michael G.S. Londesborough [a], John D. Kennedy [a,b], Ramón Macías [c], Rudolph E.K. Winter [d], Ivana Císařová [e], Pavel Kubát [f], Kamil Lang [a]

[a] Institute of Inorganic Chemistry of the AS CR, v.v.i., 250 68 Husinec-Řež, Czech Republic
[b] The School of Chemistry of the University of Leeds, Leeds, LS2 9JT, UK
[c] Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009-Zaragoza, Spain
[d] Chemistry Department, University of Missouri, St. Louis, St Louis, MO, 63102, USA
[e] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 43 Czech Republic
[f] J. Heyrovský Institute of Physical Chemistry of the AS CR, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

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ABSTRACT

The bimetalladodecaborane cluster compound [(PMe$_2$Ph)$_4$Pt$_2$B$_{10}$H$_{10}$] **1**, quantitatively reacts with EtNC at room temperature to afford [{(EtNC)(PMe$_2$Ph)$_3$}(μ-EtNC)Pt$_2$B$_{10}$H$_{10}$] **3** in which one molecule of EtNC replaces a terminal PMe$_2$Ph ligand, and a second molecule of EtNC bridges the Pt–Pt vector. The metal-bridging EtNC molecule can be ejected from **3**, either by irradiation with UV light, or via displacement with CO to form [{(EtNC)(PMe$_2$Ph)$_3$}(μ-CO)Pt$_2$B$_{10}$H$_{10}$] **4**. The CO-bridge may then in turn be replaced with SO$_2$ to give [{(EtNC)(PMe$_2$Ph)$_3$}(μ-SO$_2$)Pt$_2$B$_{10}$H$_{10}$] **5**. If **3** is allowed to react directly with SO$_2$ then the SO$_2$ molecule takes up a bridging position and the bridging EtNC displaces a terminal metal-bound phosphine to afford [{(EtNC)$_2$(PMe$_2$Ph)$_2$}(μ-SO$_2$)Pt$_2$B$_{10}$H$_{10}$] **6**. The transient absorption spectrum of **3** under UV illumination is investigated and shows that the bridging isonitrile is ejected to produce a transient spectrum very similar to that of [(PMe$_2$Ph)$_4$Pt$_2$B$_{10}$H$_{10}$] **1**. Reaction of [(PMe$_2$Ph)$_4$Pd$_2$B$_{10}$H$_{10}$] **7**, viz. the dipalladium analogue of **1**, with EtNC results in the displacement of two PMe$_2$Ph phosphine ligands forming [{(EtNC)$_2$(PMe$_2$Ph)$_2$}Pd$_2$B$_{10}$H$_{10}$] **8**, which has no bridging EtNC unit and which shows only a weak ability to form an adduct with SO$_2$. DFT calculations at the B3LYP/6-31G* level mirror the observed data well.

1. Introduction

The temporary binding of small molecules onto metal centres and metal surfaces facilitate reaction pathways otherwise denied by insurmountable energy barriers. We have pioneered the use of icosahedral bimetallic 'B-frame' compounds to reversibly, and controllably, capture small molecules across their cluster metal–metal vector [1–5]. Thus, for example, solutions of the bimetalladodecaborane [(PMe$_2$Ph)$_4$Pt$_2$B$_{10}$H$_{10}$] **1** are able to sequester O$_2$, CO and SO$_2$ across the Pt–Pt vector [1,2,4,6]. In the case of the dioxygen adduct [(PMe$_2$Ph)$_4$(μ-O$_2$)Pt$_2$B$_{10}$H$_{10}$] **2**, the sequestration is reversed by gentle heating or by purging with a stream of inert gas

[6]. The [(PMe$_2$Ph)$_4$M$_2$B$_{10}$H$_{10}$] system is convenient for tuning the sensitivity of the M–M vector towards the uptake and release of such small molecules as it comprises three components: the dimetal centre, the metal-bound ligands, and the boron cluster; each of which may be independently varied during the synthesis of the cluster compound [3,5]. For example, the bimetallic complex **1** becomes more weakly binding when one Pt centre is replaced by Pd. Thus, with [(PMe$_2$Ph)$_4$(μ-CO)PtPdB$_{10}$H$_{10}$], the bound CO moiety may subsequently be displaced by SO$_2$, irreversibly. If both platinum centres are replaced by palladium, as in [(PMe$_2$Ph)$_4$(μ-SO$_2$)Pd$_2$B$_{10}$H$_{10}$], the SO$_2$ moiety itself is now less strongly bound, and may be displaced by a stream of CO [4].

Density Functional Theory (DFT) calculation is a reliable tool in predicting, in advance of synthetic work, the effect of varying any of the three components of the system. With regard to the reversible uptake by bimetallaborane clusters of carbon monoxide, a good metric for the binding strength of the CO molecule to the cluster is the measurement of infra-red CO stretching frequency: the

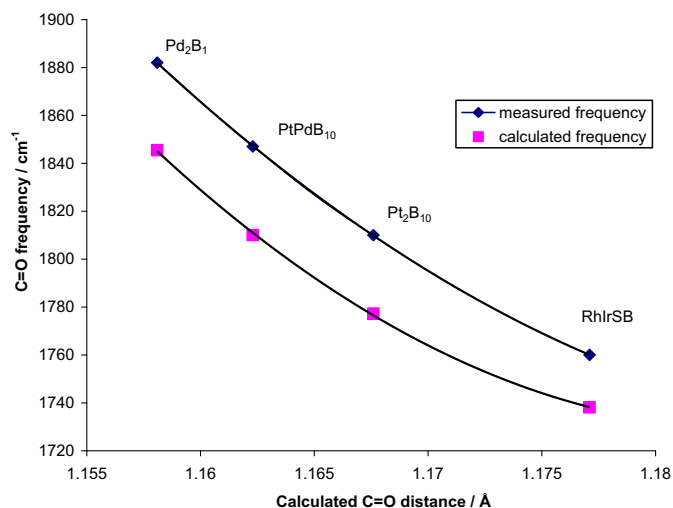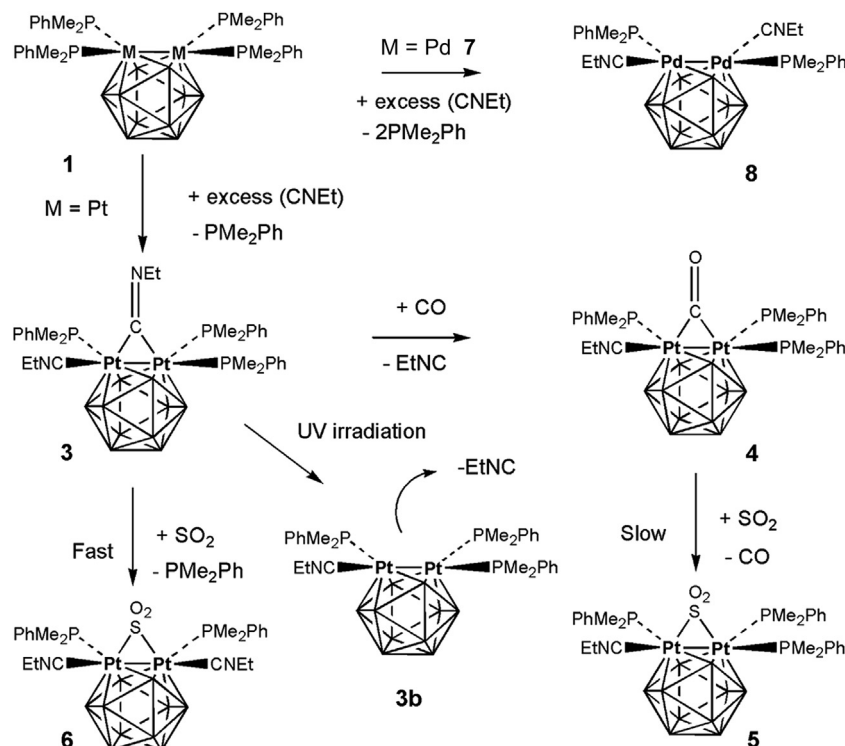**Fig. 1.** Plots of calculated C—O distances *versus* measured and calculated IR frequencies for ν(C=O) for a series of twelve-vertex bimetallaboranes [4,8]. Measured species are [(PMe₂Ph)₄(μ-CO)Pt₂B₁₀H₁₀], [(PMe₂Ph)₄(μ-CO)PdPtB₁₀H₁₀], [(PMe₂Ph)₄(μ-CO)Pd₂B₁₀H₁₀] and [(PPh₃)(PMe₃)₃(μ-CO)RhIrSB₉H₉]. The corresponding model calculated species are [(PH₃)₄(μ-CO)Pt₂B₁₀H₁₀], [(PH₃)₄(μ-CO)PdPtB₁₀H₁₀], [(PH₃)₄(μ-CO)Pd₂B₁₀H₁₀] and [(PH₃)₄(μ-CO)RhIrSB₉H₉].

well by the DFT calculations, although the absolute frequencies differ by 30−40 cm^{-1} in each case.

The NC units of isonitriles are isoelectronic and isolobal with carbonyl units and isonitriles form complexes with transition elements in both low and normal oxidation states. Within the low-valent category, there is similarity to the carbon monoxide complexes in terms of both structure and reactivity, with isonitriles being generally regarded as better σ donors and weaker π acceptors than carbon monoxide [9]. This similarity between carbon monoxide and isonitrile compounds suggests that isonitriles would show a similar behaviour to CO with regard to its binding at the M—M vector in the types of bimetallic borane cluster mentioned above. In terms of DFT predictive work, a good correlation between the calculated and experimentally measured IR carbonyl stretching frequencies in the series of bimetalladodecaborane cluster compounds (Fig. 1) and thence the reliable estimation of the cluster-to-molecule bonding strength implied by these values, encouraged us to use the DFT method to probe the theoretical capture of other small molecules before substantiating the computational predictions by targeted syntheses and spectroscopic and spectrometric characterisation. For isonitriles, in addition to the calculation of R—N≡C—M bonding distances, a useful gauge to the strength of coordination of any isonitrile moiety to an M—M vector might be manifested in the (μ-C=N—R) angle, where a smaller angle indicates a stronger binding. This is a metric which would be easily comparable with accurately determined experimental values from single-crystal X-ray diffraction analyses. This would differ from the case with CO, where small changes in the C=O distances would not be sufficiently accurately measurable from X-ray diffraction results. Thus, for calculations at the B3LYP/6-31G* level for the model compounds [(PH₃)₄(μ-EtNC)M₂B₁₀H₁₀], where M₂ = Pt₂ and Pd₂, the results gave the quite different (μ-C=N-R) angles of 135.6° and 175.8° for the diplatinum and dipalladium species, respectively, a difference which should be readily apparent from the results of

stronger the CO-metal interaction, the longer the C—O distance and the lower the frequency for the C=O bond. For a series of equivalent phosphine-ligated species of model bimetallaboranes, [(PH₃)₄(μ-CO)Pt₂B₁₀H₁₀], [(PH₃)₄(μ-CO)PdPtB₁₀H₁₀], [(PH₃)₄(μ-CO)Pd₂B₁₀H₁₀] and [(PH₃)₄(μ-CO)RhIrSB₉H₉] [4,8], Fig. 1 shows the correlation between the plot of the calculated C=O distance *versus* the measured ν(C=O) infrared stretching frequency and the plot of the fully calculated ν(C=O) *versus* the calculated C=O distances. It can be seen that the experimentally obtained sequence is mirrored

Scheme 1.