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Nickel-Molybdenum and Nickel-Tungsten Dithiolates: Hybrid Models for Hydrogenases and Hydrodesulfurization

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The heterobimetallic complexes [(dppe)Ni(pdt)Mo(CO)₄], [(dcpe)Ni(pdt)Mo(CO)₄], [(dppe)Ni(pdt)W(CO)₄] and [(dcpe)-Ni(pdt)W(CO)₄] {dppe = Ph₂P(CH₂)₂PPh₂; dcpe = Cy₂P(CH₂)₂-PCy₂; pdt²⁻ = ⁻S(CH₂)₃S⁻} have been prepared and structurally characterized. The internuclear separation in these Ni^{II}M⁰ species is highly sensitive to diphosphine basicity and is smallest in the dppe complexes wherein the planar Ni centres are electron-poor and require interaction with the group 6 metal. The Ni^{II}W⁰ species [(dppe)Ni(pdt)W(CO)₄] was converted into its stable conjugate acid [(dppe)Ni(pdt) HW(CO)₄]⁺, a rare example of a nickel–tungsten hydride. This Ni^{II}HW^{II} complex is an electrocatalyst for H⁺ reduction and is relevant to both biological and synthetic H₂-processing catalysts.

Introduction

The isolation of many commodity hydrocarbons relies on hydrogenolysis of C–N/S bonds, reactions often mediated by $Mo_xW_{1-x}S_2$ layers promoted by Co or Ni.^[1,2] The effectiveness of these heterogeneous catalysts has inspired the synthesis of molecular analogues, one promising route to which involves combination of Mo/W(CO)_n electrophiles with square-planar Ni^{II} alkylthiolates. Indeed, complexes of the type [Ni^{II}L₂(SR)₂] are versatile metalloligands with basicities comparable to that of 2,2'-bipyridine.^[3] For example, Ni^{II} diaminodithiolates have been incorporated into several multinuclear species,^[4] including [*N*,*N*'-bis(2-sulfidoethyl)diazacyclooctane]NiM(CO)₄ (1: M = Mo; 2: M = W),^[5] which features a topical NiS₂M core (Figure 1). Of comparable basicity are Ni^{II} diphosphinodithiolates – these



Figure 1. Examples of thiolate-bridged Ni complexes of group 6 tetracarbonyls.

also form stable Ni^{II}Mo⁰ species such as tetracarbonyl 3.^[6]

The present study makes use of the modularity with which one can prepare $[L_2Ni(SR)_2M(CO)_4]$ complexes. Employed here are $[Ni(dppe)(pdt)]^{[7]}$ and $[Ni(dcpe)(pdt)]^{[8]}$ building blocks, which, while similar to the Ni^{II} fragment in **3**, retain some conformational flexibility when ligated to another metal. Accordingly, such units have recently been incorporated into many bimetallics, including H₂-evolving catalyst $[(dppe)Ni(pdt)Fe(CO)_3]$ (**4**, Scheme 1).^[9]



Scheme 1. Isomers and oxidation states in $[(dppe)M(pdt)Fe(CO)_3]$ species.

Rotation of the dppe ligand in **4** is associated with fluxionality between a metal–metal bonded "resting state" and a 2e[–] mixed-valence state with enhanced proton affinity.^[10] Complexes like **4** are among the few functional synthetic models for nickel–iron hydrogenase, a key enzyme in anaerobic H₂ metabolism and an aspirational target for synthetic catalysts.^[11] Described now are NiS₂M (M = Mo, W) derivatives that blend hydrodesulfurization and hydrogenase themes into a promising catalytic motif.

Results and Discussion

Treatment of the labile precursors cis-[Mo(CO)₄(piperidine)₂] and cis-[W(CO)₄(piperidine)₂]^[12] with nucleophiles

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 $[(dppe)Ni(pdt)]^{[7]}$ and $[(dcpe)Ni(pdt)]^{[8]}$ in CH₂Cl₂ afforded the four new bimetallics $[(dppe)Ni(pdt)Mo(CO)_4]$ (7), $[(dcpe)Ni(pdt)Mo(CO)_4]$ (8), $[(dppe)Ni(pdt)W(CO)_4]$ (9) and $[(dcpe)Ni(pdt)W(CO)_4]$ (10) in good yields; heating is required in the latter two cases (Scheme 2). Robust and crystalline, the complexes are unaffected by air for short periods, although their solutions are more sensitive.



Scheme 2. Preparation of $[(diphosphine)Ni(pdt)M(CO)_4]$ (M = Mo, W).

In line with the pseudo- $C_{2\nu}$ symmetry of the M(CO)₄ fragments, IR spectra of tetracarbonyls **7–10** in CH₂Cl₂ solution feature four ν_{CO} bands, the energies of which support a Ni^{II}M⁰ oxidation state formalism (Table 1 and Figure 2). The average ν_{CO} energies of the Ni^{II}W⁰ complexes are ca. 8 cm⁻¹ lower than those of Ni^{II}Mo⁰ species, consistent with increased π -backdonation in the former case. The energies also decrease by ca. 5 cm⁻¹ when the more basic ligand dcpe is employed in place of dppe; a similar shift is observed for complex **4** and its dcpe congener.^[8] Lastly, the single, sharp ³¹P NMR resonances observed in each case are consistent with a somewhat rigid structure of C_s symmetry.

Table 1. CO-stretching frequencies and Ni–M separations in tetra-carbonyls.

Compound	$v_{\rm CO} [{\rm cm}^{-1}]$	r(NiM) [Å]
[N,N'-bis(2-sulfidoethyl)-	2002, 1884,	_
diazacyclooctane]NiMo(CO) ₄ (1)	1861, 1824 ^[a]	
[N,N'-bis(2-sulfidoethyl)]	1995, 1871,	3.35
-diazacyclooctane]NiW(CO) ₄ (2)	1853, 1819 ^[a]	
$Ni[Ph_2P(CH_2)_2S]_2Mo(CO)_4$ (3)	2006, 1883, 1844 ^[b]	2.998
$[(dppe)Ni(pdt)Mo(CO)_4]$ (7)	1997, 1896,	2.903
	1856, 1839 ^[c]	
$[(dcpe)Ni(pdt)Mo(CO)_4]$ (8)	1995, 1886,	3.124
	1858, 1830 ^[c]	
$[(dppe)Ni(pdt)W(CO)_4]$ (9)	1991, 1885,	2.907
	1846, 1832 ^[c]	
$[(dcpe)Ni(pdt)W(CO)_4]$ (10)	1989, 1875,	3.284
	1848, 1825 ^[c]	
[(dppe)Ni(pdt)HW(CO) ₄]BF ₄ ([9H]BF ₄)	2076, 2018,	_
	1996,	
	1934 ^[c]	

[a] Measured in DMF (Ref.^[5]). [b] Measured in THF (Ref.^[6]), two bands are superimposed at 1844 cm⁻¹. [c] Measured in CH₂Cl₂.

The bimetallics crystallized upon diffusion of pentane vapour into CH_2Cl_2 solutions of the complexes. In each case, the single crystals were amenable to X-ray diffraction; the structures of NiMo species 7 and 8 are presented in



Figure 2. IR spectra (v_{CO} region) of NiM tetracarbonyls prepared in this work.

Figure 3, while those of NiW species 9 and 10 are in Figure 4 (metrics are summarized in the Supporting Information).



Figure 3. ORTEP diagrams of $[(dppe)Ni(pdt)Mo(CO)_4]$ ·CH₂Cl₂ (top) and $[(dcpe)Ni(pdt)Mo(CO)_4]$ (bottom) with ellipsoids drawn at the 40% probability level. Solvate, H atoms and Cy ring disorder are omitted for clarity.

The solid-state structures of the complexes each feature a square-planar Ni site linked to octahedral M through the pdt^{2-} ligand. Although the NiS₂M "butterfly" cores are smaller in the respective NiMo species, in all cases the internuclear separation exceeds the sum of the covalent radii (Ni 1.24 Å, Mo 1.54 Å, W 1.62 Å).^[13] This indicates negligible bonding between the centres, which, when taken with the planarity of the Ni site, further suggests that the com-





Figure 4. ORTEP diagrams of $[(dppe)Ni(pdt)W(CO)_4]$ ·CH₂Cl₂ (top) and one of two independent complexes in $[(dcpe)Ni(pdt)-W(CO)_4]$ ·CH₂Cl₂ (bottom) with ellipsoids drawn at the 50% probability level. Solvate and H atoms (and Ph and CO disorder in **9**) are omitted for clarity.

plexes are indeed 2e- mixed-valence Ni^{II}M⁰ species. Comparing structural metrics of dppe and dcpe congeners provides insight into the electronic demands of the Ni^{II} centre. For example, [(dppe)Ni(pdt)Mo(CO)₄] features a compressed butterfly core, likely a result of the electron-poor Ni^{II} site requiring some interaction with Mo⁰ and the most proximal CO ligand. In contrast, the metal centres in $[(dcpe)Ni(pdt)Mo(CO)_4]$ are substantially (0.221 Å) further apart, highlighting the role of diphosphine basicity in attenuating Ni electrophilicity. This effect is even more pronounced in the NiW complexes; the metals in [(dppe)- $Ni(pdt)W(CO)_4$ are 0.377 Å closer together than those in [(dcpe)Ni(pdt)W(CO)₄]. Given the geometry of the four complexes, the steric profiles of the Cy and Ph groups are unlikely to influence internuclear separations, and these trends can thus be ascribed to stereoelectronic effects.

The redox properties of **7** and **9** were investigated by cyclic voltammetry; two waves are observed in each case. Ni^{II}Mo⁰ complex **7** and Ni^{II}W⁰ complex **9** (pseudo-reversibly) oxidize to Ni^{II}M^I species at -0.205 and -0.250 V vs. Fc^{0/+}, respectively; the wave is more cathodic for the electron-rich NiW species. Irreversible reductions of **7** and **9** occur at -1.841 and -1.809 V, respectively.

The Ni^{II}M⁰ species 7–10 are significant in light of our recent work on tricarbonyls $[(dppe)Ni(pdt)Fe(CO)_3]$ (4), $[(dppe)Pd(pdt)Fe(CO)_3]$ (5) and $[(dppe)Pt(pdt)Fe(CO)_3]$

(6).^[10] Although 4 was characterized as a Ni^IFe^I species, its catalytic cycle likely involves isomerization to the more basic Ni^{II}Fe⁰ rotamer. While similar dynamics are evident for 5, the PtFe species 6 resembles the present work in that the group 10 metal remains in the divalent state. This builds on the analogy between 14 valence electron $Fe^{0}(CO)_{3}$, Mo⁰(CO)₄ and W⁰(CO)₄ fragments, which each serve as useful spectroscopic handles.

The propensity of iron tricarbonyls 4, 5 and 6 to form hydrides^[10] prompted investigation into whether protonation of the present group 6 tetracarbonyls would also proceed. Stable examples of heptacoordinate carbonyl hydrides of Mo^{II} and W^{II} are known,^[14,15] and complexes 7 and 9 were examined here. Treatment of Ni^{II}Mo⁰ complex 7 with a tenfold excess of HBF4·OEt2 in CD2Cl2 induced formation, albeit incomplete, of a Ni^{II}HMo^{II} product formulated as [7H]⁺. While the ³¹P signal shifts downfield by only 6 ppm (the Ni oxidation state is unchanged upon Mo⁰ protonation), a high-field ¹H NMR resonance at $\delta = -4.05$ ppm is characteristic of a metal hydride. The low basicity of 7 contrasts that of its NiW congener 9 - the latter complex is readily protonated by a single equivalent of HBF₄·OEt₂. The protonation of 9 in CH₂Cl₂ induces a colour change from green to orange, as well as a shift of the ³¹P NMR resonance from 55.4 to 58.2 ppm (Scheme 3). Again, most diagnostic of the H⁻ ligand is a ¹H NMR signal at -3.59 ppm. No ³¹P coupling could be resolved, indicating that H- is bound to W and interacts negligibly with Ni. While the Ni^{II}HW^{II} product [9H]⁺ is stable towards excess acid (allowing electrocatalytic studies, vide infra), it is readily deprotonated by excess Et₂O, indicating that 9 is still not very basic. ESI-MS analysis of acidified 9 revealed ions at m/z = 859.1 and 831.1, with isotope patterns consistent with formulations $[9H]^+$ and $[9H - CO]^+$, respectively (decarbonylated fragments are common ESI products). A molecular ion at m/z = 860.2 was observed when protonation was performed in the presence of CD₃OD.



Scheme 3. Protonation of $Ni^{II}W^0$ complex 9 affords the $Ni^{II}HW^{II}$ species [9H]BF₄.

The product [9H]BF₄ is a stable solid, the ν_{CO} pattern of which is different to that of 9, consistent with a change in coordination geometry. The mean energy of the four ν_{CO} bands (2006 cm⁻¹) for [9H]BF₄ is 118 cm⁻¹ greater than that of 9, a similar change (119 cm⁻¹) having been obtained for the protonation of a related (PNP)W⁰(CO)₃ complex.^[14]

Returning to the analogy with iron tricarbonyls, the hydrido in $[(dppe)Pt(pdt)HFe(CO)_3]^+$ ([6H]⁺) is tightly bound to Fe, quite distinct from the situation in $[(dppe)Ni(pdt)-HFe(CO)_3]^+$ ([4H]⁺), in which H⁻ is more evenly shared. Thus, parallels between 2e⁻ mixed-valence complexes 6 (Pt^{II}Fe⁰) and 9 (Ni^{II}W⁰), as well as hydrides [6H]⁺ and



 $[9H]^+$ become clear. The present work points to a trend that stems, at least in part, from the basicity of zerovalent metal centres: protonation of 2e⁻ mixed-valence M^{II}M'⁰ species can afford asymmetrically-bound Ni^{II}HM'^{II} hydrido complexes, while protonation of metal–metal bonded M^IM'^I cores often results in more symmetric, bona fide μ -hydrido species.^[16]

Hydride $[9H]^+$ exhibits an irreversible reduction at -1.28 V associated with the formation of H₂ and 9, the latter evidenced by the appearance of the $9^{0/+}$ wave at -0.25 V. The activity of $[9H]^+$ toward H⁺ reduction was probed by cyclic voltammetry. Consistent with $[9H]^+$ acting catalytically, titration with HBF₄·OEt₂ resulted in an increase in the reductive current, with an initial linearity indicating a process second order in $[H^+]$ (Figure 5).



Figure 5. Cyclic voltammograms of $[9H]BF_4$ in the presence of HBF₄·OEt₂ (molar equivalents are to the left of each trace). Potentials are relative to the Fc^{0/+} wave at 0 V, with conditions detailed in the Supporting Information. Inset: changes in current as a function of acid concentration.

A defining parameter for electrocatalysis is the potential at which half of the catalytic current is reached ($E_{cat/2} =$ -1.21 V). Further, the ratio of the maximum current in the presence and absence of acid ($i_c/i_p = 15.4$) was used to determine the turnover frequency of [9H]⁺ (TOF = 47 s⁻¹).^[17,18] While much slower than the nickel–iron hydrogenases (TOF \approx 700 s⁻¹),^[19] it is envisaged that the tetracarbonyls described here possess the requisite electrophilicity to undergo ligand-substitution reactions and afford more Brønsted basic and active catalyst species.

Conclusions

A family of Ni^{II}Mo⁰ and Ni^{II}W⁰ tetracarbonyls has been prepared, and the effects of ligand basicity and metal acidity were investigated by IR spectroscopy and X-ray structural analysis. While NiMn thiolates,^[20] as well as NiFe^[8,21–23] and NiRu^[24–27] species (including hydrides) are promising H₂-processing catalysts, this work focuses on the earlier metals Mo and W. These group 6 metals allow access to dinuclear species with different modes of substrate binding though seven-coordinate species, as exemplified in the formation of a NiW hydrido complex. While $[9H]^+$ has modest activity for H⁺ reduction, compounds of the present type have readily tunable redox properties and pK_a values, and further investigations into such motifs may well be profitable.

Experimental Section

Synthetic procedures for 7-10 and $[9H]BF_4$, structural details, IR, NMR and mass spectra, and electrochemical data are available in the Supporting Information for this paper.

CCDC-1409249 (7), CCDC-1409250 (8), CCDC-1409251 (9) and CCDC-1409252 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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