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A hemilabile manganese(i)–phenol complex and its coordination induced O–H bond weakening†

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The known compound $K[(PO)_2Mn(CO)_2]$ ($PO = 2-((diphenylphosphino)methyl)-4,6-dimethylphenolate$) (**1**) was protonated to form the new Mn(i) complex $(HPO)(PO)Mn(CO)_2$ (**H1**) and was determined to have a pK_a approximately equal to tetramethylguanidine (TMG). The reduction potential of **K1** was determined to be -0.58 V vs. Fc/Fc^+ in MeCN and allowed for an estimation of an experimental O–H bond dissociation free energy ($BDFE_{O-H}$) of 73 kcal mol⁻¹ according to the Bordwell equation. This value is in good agreement with a corrected DFT computed $BDFE_{O-H}$ of 68.0 kcal mol⁻¹ (70.3 kcal mol⁻¹ for intra-molecular H-bonded isomer). The coordination of the protonated O-atom in the solid-state **H1** was confirmed using FTIR spectroscopy and X-ray crystallography. The phenol moiety is hemilabile as evident from computation and experimental results. For instance, dissociation of the protonated O-atom in **H1** is endergonic by only a few kcal mol⁻¹ (DFT). Furthermore, **1**⁻ and other Mn(i) compounds coordinated to **PO** and/or **HPO** do not react with MeCN, but **H1** reacts with MeCN to form **H1+MeCN**. Experimental evidence for the solution-bound O-atoms of **H1** was obtained from ¹H NMR and UV-vis spectroscopy and by comparing the electronic spectra of *bona fide* 16-e⁻ Mn(i) complexes such as $[(PNP)Mn(CO)_2]$ ($PNP = ^-N(CH_2CH_2(P^iPr_2))_2$) and $[(Me_3SiOP)(PO)Mn(CO)_2]$ (**Me3Si1**). Compound **H1** is only meta-stable ($t_{1/2}$ 0.5–1 day) and decomposes into products consistent with homolytic O–H bond cleavage. For instance, treatment of **H1** with TEMPO resulted in formation of TEMPOH, free ligand, and $[Mn^II\{(PO)_2Mn(CO)_2\}_2]$. Together with the experimental and calculated weakened $BDFE_{O-H}$, these data provide strong evidence for the coordination and hemilability of the protonated O-atom in **H1** and represents the first example of the phenolic Mn(i)–O linkage and a rare example of a “soft-homolysis” intermediate in the bond-weakening catalysis paradigm.

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Introduction

The proton coupled electron transfer (PCET) chemistry induced by coordination of metal ions to phenolic O–H moieties is an important process in nature.^{1,2} Additionally, others have recently taken advantage of “soft homolysis”, or coordination induced X–H (X = O, N, etc.) bond weakening, for energy and chemical synthesis.^{3–7} However, there are few reports on the thermodynamics of the O–H bond on phenolic ligands coordinated to a metal because phenols are weak ligands,⁸ and covalent metal–Ph(O)H linkages are rare. Most metal–Ph(O)H are loosely bound ionic high-spin inorganic

complexes, and the low-spin organometallic complexes contain 2nd and 3rd row transition-metal centers (for example, Mo,⁹ Ru,¹⁰ Rh,¹¹ and Ir¹²). Even high-spin compounds tend to deprotonate to give a phenolate-metal complex or, in the case of metallo-enzymes like transferrin,^{1,2} undergo reductive PCET thus making the metastable phenol-bound metal complex difficult to isolate and characterize.^{9,12c} Our ongoing efforts in studying O–H bond weakening in Mn(i) complexes and also development of phenolate-phosphine ligands led us to prepare a unique set of Mn(i)-phenol and phenolate complexes that are amenable to this study. As such, this report details a systematic thermodynamic evaluation of the first low-spin 1st-row transition metal–Ph(O)H motif. Herein, we describe the preparation of a Mn(i)–Ph(O)H complex, $(HPO)(PO)Mn(CO)_2$ (**H1**), and discuss its solution and solid-state structure to demonstrate that the O-atom of the phenol is indeed coordinated to the Mn(i) center. This discussion then leads to an evaluation of the O–H bond dissociation free energy that is weakened from a free phenol as a result of the coordination.

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Results and discussion

Protonation of K[1] in non-coordinating solvents

In a previous report, we described the synthetic route to the anionic dicarbonyl Mn(I) complex supported with two PO ligands $[(\text{PO})_2\text{Mn}(\text{CO})_2]^-$ ($[1]^-$), where **PO** = 2-((diphenylphosphino)methyl)-4,6-dimethylphenolate; both the potassium and manganese(II) salt of $[1]^-$ were prepared (*i.e.* K[1] and $\text{Mn}^{\text{II}}[1]_2$).¹³ Protonation of K[1] with one or more equivalents of lutidinium tetrafluoroborate ($[\text{Lt-H}]\text{BF}_4$) in DCM led to generation of a dark orange complex (**HPO**)(**PO**) $\text{Mn}(\text{CO})_2$ (**H1**), along with the formation of white ppt (KBF_4) (Scheme 1).¹⁴ Monitoring the reaction with $^{31}\text{P}\{^1\text{H}\}$ NMR showed complete conversion from K[1] ($^{31}\text{P}\{^1\text{H}\}$ NMR δ 55.2 ppm) to **H1** ($^{31}\text{P}\{^1\text{H}\}$ NMR δ 54.3 ppm) (Fig. S2†). The ATR-FTIR spectrum of **H1** revealed that it is a dicarbonyl complex ($\nu_{\text{CO}} = 1924, 1844 \text{ cm}^{-1}$) with an OH stretch at 3480 cm^{-1} (Fig. S3†). The CO stretches are shifted to higher energy compared to that of K[1] ($\nu_{\text{CO}} = 1894, 1802 \text{ cm}^{-1}$). The ^1H NMR spectrum of **H1** contains a peak at δ 2.69 ppm that integrates to one proton, which is assigned to the OH group on the phenol (Fig. S1a†). This assignment was validated by the absence of this peak in the ^1H NMR spectrum of the deuterated analog ($d_1\text{-H1}$) (Fig. S1b†). The ATR-FTIR of $d_1\text{-H1}$ showed the presence of a shifted OD stretch at 2580 cm^{-1} ($\nu(\text{OH})/\nu(\text{OD})$ calc. = 1.37, exp. = 1.35) (Fig. S4†). Crystals suitable for diffraction were obtained using the deuterated analog $d_1\text{-H1}$ (Fig. 1).¹⁴ The XRD structure revealed a coordination environment similar to that of K[1]. While K[1] has a symmetrical structure with nearly equivalent Mn–O distances (2.075 and 2.068 Å), **H1** is comparatively asymmetric with nonequivalent Mn–O distances (2.210 and 2.014 Å) that is consistent with one of the O-atoms being protonated.

A DFT computed structure of **H1** (see Fig. S5†) is consistent with the XRD structure in which the phenol group coordinates

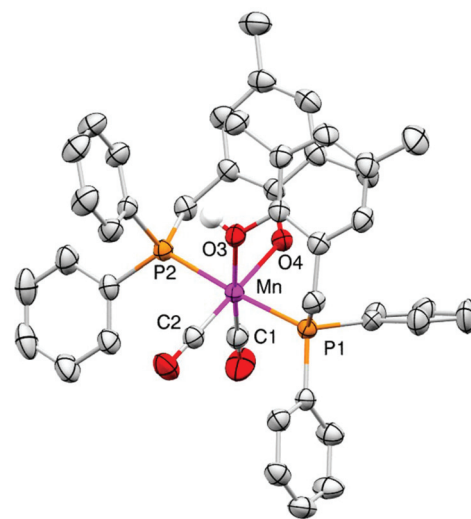
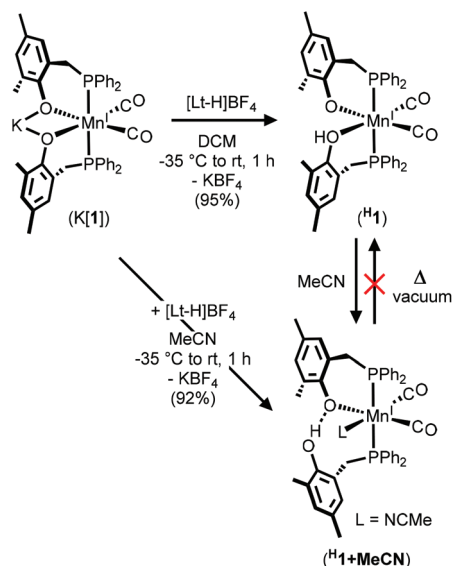


Fig. 1 Molecular structure of **H1** determined from XRD (ellipsoids at 50% probability). H-atoms attached to carbon not shown. Selected distances (Å): Mn–O4 = 2.014(1); Mn–O3 = 2.210(1); O3...O4 = 2.854(2); Mn–C1 = 1.762(2); Mn–C2 = 1.784(2); Mn–P1 = 2.292(1); Mn–P2 = 2.279(1).

to the vacant site *trans* to one of the CO ligands and *cis* to the phenolate and two phosphine ligands. Like the XRD structure, the DFT structure suggests different environments for the two phosphine ligands. Note that a different isomer was computed for **H1** in a previous report where the phenolic H-atom is engaged in an intramolecular H-bonding interaction ($\text{O}_a\text{--H}\cdots\text{O}_b$).¹³ This H-bonded isomer of **H1** is 2.7 kcal mol^{−1} lower in energy than the one without the H-bonding interaction (gas phase and in toluene).

It is possible that the solid-state and computed structures do not accurately describe the solution-state structure of **H1**. However, the OH ^1H -NMR chemical shift and ν_{OH} from FTIR are near those for the tetrameric Mn complex $[\text{Mn}(\text{CO})_3(\mu_3\text{--OH})]_4$ with bridging Mn–OH moieties.¹⁵ The similarities indicate that the OH group is strongly interacting with a Mn(I) center, but the single $^{31}\text{P}\{^1\text{H}\}$ peak indicates a weak H-bonding interaction ($\text{O}_a\text{--H}\cdots\text{O}_b$) or possible fluxional position of the proton (Fig. S2a†) in the solution state; NMR and UV-vis spectra of **H1** at low temperature were unchanged from room temperature.

An alternative solution-state structure is one where the phenol arm has dissociated away from the Mn(I) center resulting in a *bona fide* 16-e[−] 5-coordinate complex. This isomer of **H1** (**H1'**) was computed as a local minimum using DFT, but it is 0.6 kcal mol^{−1} higher in energy than the one computed for **H1** and 3.3 kcal mol^{−1} higher than the intramolecular H-bonded isomer of **H1** (Scheme 4). Since VT NMR and UV-vis of **H1** did not indicate changes, we suspect that the H-bonded isomer of **H1** is predominant in the solution-state. Furthermore, as we will discuss, the electronic spectrum of **H1** appears to indicate that the O–H moiety is coordinated to Mn to effectively mask a 16-e[−] complex, rather than the dissociated 16-e[−] complex **H1'**.



Scheme 1 Synthesis of **H1** and **H1+MeCN** from K[1].

Protonation of K[1] in coordinating solvents

Repeating the same protonation reaction of K[1] in acetonitrile led to dissociation of the protonated phenol group and association of a solvent molecule to give the neutral yellow compound (HPO)(PO)Mn(CO)₂(MeCN), (^H1+MeCN). This compound is isostructural with our previously reported complex (HPO)(PO)Mn(CO)₃, (^H1+CO).¹³ The OH stretch in the ATR-FTIR spectrum (Fig. S7†) of ^H1+MeCN is broad and shifted to lower energy, 2350 cm⁻¹, suggesting a strong H-bond interaction with the bound phenolate oxygen. ³¹P{¹H} NMR spectrum of ^H1+MeCN showed two broad peaks at δ 78.5 and 64.9 ppm corresponding to the bidentate PO ligand and the monodentate HPO ligand, respectively (Fig. S6†). These spectroscopic data closely match those associated with ^H1+CO, which showed a similar broad OH peak at around 2500 cm⁻¹ in the ATR-FTIR spectrum. The ¹H-NMR spectrum of ^H1+MeCN was uninformative due to broadening from paramagnetic byproducts.¹⁴ Crystals suitable for XRD were obtained (Fig. 2). While addition of MeCN to solid ^H1 led to the formation of ^H1+MeCN, the reverse reaction of removing a solvent molecule *in vacuo* from solid ^H1+MeCN to form ^H1 did not occur (up to 75 °C, <1 mTorr). Complexes ^H1+CO and [1]⁻ do not react with MeCN, thus providing some evidence that the ROH in ^H1 group is hemilabile to allow for the facile coordination of MeCN.

Hemilability of the phenol ligand in ^H1

Considering the weak binding of phenolic groups to metals, compound ^H1 can be thought of as a masked 16-e⁻ Mn(i) complex. The UV-vis spectrum of [1]⁻ and other 18-e⁻ complexes prepared with HPO all contain a single large feature λ_{max} ≈ 400–500 nm, giving these complexes a yellow to orange color. However, ^H1 contains a new, but very weak, shoulder at 570 nm that is not present in any of the other complexes we observed so far and indicates a weakened ligand field (Fig. 3).¹⁶ We hypothesized that replacing the proton in ^H1 with other bulky electrophiles should allow us to generate unmasked 16-e⁻ complexes. Thus, we treated K[1] with

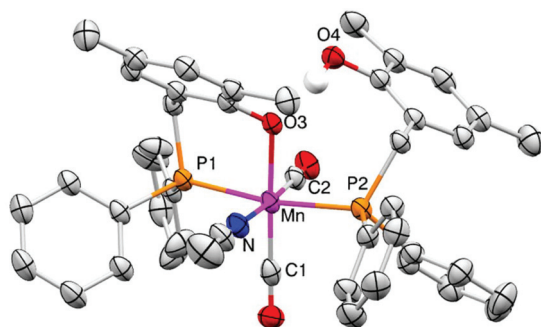


Fig. 2 Molecular structure of ^H1+MeCN determined from XRD (ellipsoids at 50% probability). H-atoms attached to carbon not shown. Selected distances (Å): Mn–O3 = 2.068(1); O3...O4 = 2.558(2); Mn–C1 = 1.778(2); Mn–C2 = 1.814(2); Mn–P1 = 2.3021(6); Mn–P2 = 2.3326(6); Mn–N = 1.997(2).

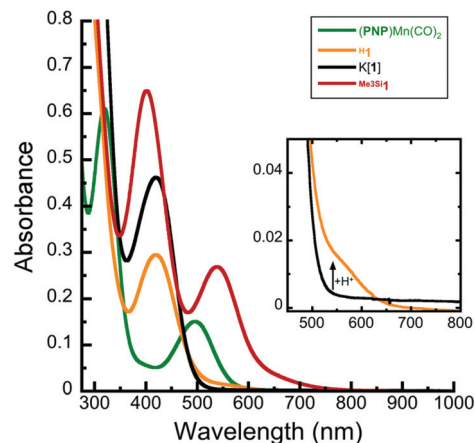
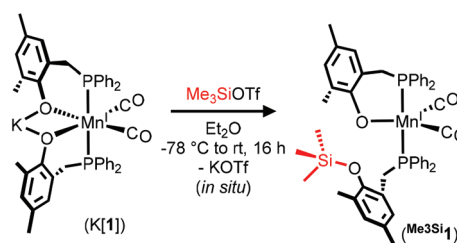


Fig. 3 UV-vis spectra of Mn(i) dicarbonyl compounds in benzene: λ_{max} K[1] = 420 nm (ε = 2700 M⁻¹cm⁻¹); ^H1 = 420 nm (shoulder = 570 nm); Me₃Si¹ = 402 nm, 540 nm; (PNP)Mn(CO)₂ = 319 nm, 496 nm. Inset shows the shoulder at 570 nm. PNP = ⁻N{CH₂CH₂(PⁱPr₂)₂}.¹⁷



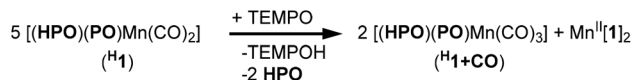
Scheme 2 Synthesis of Me₃Si¹ from K[1].

Me₃SiOTf to yield a new deep-red compound *in situ*, assigned as (Me₃SiOP)(PO)Mn(CO)₂ (Me₃Si¹) (Scheme 2). The ³¹P{¹H} NMR spectrum showed two peaks at δ 51.7 and 51.9 ppm (Fig. S8†), and the ATR-FTIR spectrum revealed a dicarbonyl moiety (1925, 1851 cm⁻¹) (Fig. S9†), consistent with our assignment. Interestingly, the UV-vis spectrum of Me₃Si¹ contains two peaks at 400 and 550 nm, a feature that matches closely with Boncella's 16-e⁻ Mn(i) complex (PNP)Mn(CO)₂ (PNP = ⁻N{CH₂CH₂(PⁱPr₂)₂}),¹⁷ suggesting the true, unmasked 16-e⁻ nature of Me₃Si¹ (Fig. 3). These changes in electronic structure are also consistent with those observed by others studying hemilabile Mn(i) and Ru(ii) complexes.^{16,18,19}

Collectively, the chemistry of ^H1 is consistent with a weakly coordinated, hemilabile Mn(i)-phenol complex. All spectroscopic (XRD, UV-vis, NMR, FTIR) point towards the phenol O-atom as coordinated in the solid and solution state, and DFT supports an uphill dissociation (≈1–3 kcal mol⁻¹) to form a dissociated species as a local minimum. Furthermore, the coordination of MeCN to ^H1, but not ^H1+CO or [1]⁻, indicates that the phenol ligand undergoes facile ligand substitution.

Metastability of ^H1

Both ^H1 and ^H1+MeCN are unstable and slowly convert into ^H1+CO and other products regardless of solvent (DCM, MeCN, THF, toluene) with a half-life of about 0.5–1 day.¹⁴ A similar

Scheme 3 H-Atom transfer from H1 to TEMPO.

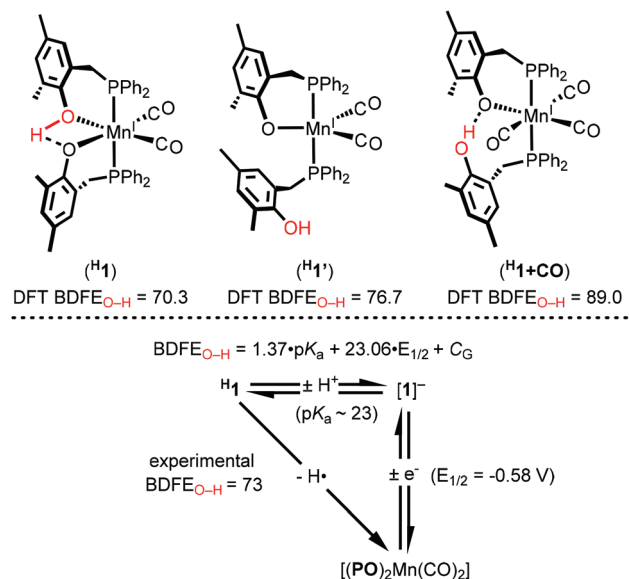
degradation pattern was observed for a monocarbonyl d^6 Mo hemilabile phenol complex that decomposed into a dicarbonyl by an unknown path.⁹ The conversion to $\text{H1}+\text{CO}$ appears to be linked to trace oxygen, but was initially puzzling since it is not a balanced reaction and since PCET and electron transfer between H1 and O_2 are both endergonic (*vide infra*). Free ligand is observed ($^{31}\text{P}\{^1\text{H}\}$ NMR δ -17.4 ppm), but there is no precipitate. We rationalized that the coordination of the phenolic O-H group to Mn(I), which is unprecedented, results in a weakened O-H bond and is responsible for the homolytic instability of H1 .

We tested this hypothesis by addition of weak H-atom abstractors to H1 . For instance, H1 in DCM or toluene was treated with TEMPO and the products were analyzed using ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, ATR-FTIR, and headspace GC analysis (Fig. S10†). The ^1H NMR analysis showed the presence of TEMPOH, $\text{H1}+\text{CO}$, and HPO in 1:2:2 ratio. Additionally, the ATR-FTIR spectrum revealed the presence of a previously reported compound $\text{Mn}^{\text{II}}[\text{1}]_2$, which is a paramagnetic trinuclear complex where a tetrahedral Mn^{II} ion links two $[\text{1}]^-$ molecular anions through the phenolate O-atoms.¹³ No gaseous products were detected using headspace GC analysis. A balanced reaction for this H-atom transfer reaction from H1 to TEMPO is shown in Scheme 3.

Interestingly, the reaction with H1 and TEMPO did not afford a complete O-H bond homolysis reaction. As we will show later, the computed $\text{BDFE}_{\text{O-H}}$ of H1 is 2 kcal mol $^{-1}$ higher than TEMPO ($\text{BDFE}_{\text{O-H}} = 66$ kcal mol $^{-1}$), so unless the resulting Mn(II) species is unstable, the equilibrium established between H1 and TEMPO will lie towards the left; as will be described later, the Mn(II) species is indeed unstable and therefore consistent with the observed reactivity. However, H1 rapidly reacts with O_2 to form $\text{H1}+\text{CO}$ and other products. Although instability of organometallics with O_2 is not unusual, H1 is significantly more reactive toward O_2 than other Mn(I) PO or HPO complexes. Since the OH bond in O_2H (45 kcal mol $^{-1}$)²⁰ is even weaker than TEMPOH, the homolysis mechanism is probably not a straightforward simple H-atom transfer with O_2 and instead must involve additional processes, such as coordination of the H-atom acceptor or coupling to rapid and favorable secondary decomposition reactions. Nevertheless, the general instability of H1 is consistent with other unstable d^6 M-Ph(O)H complexes,^{9,12c} and the reactivity is indicative of a weakened O-H bond, induced by the coordination of the phenol group to the metal and our efforts in determining the extent of this bond weakening is described next.

Estimating the $\text{BDFE}_{\text{O-H}}$ in H1

Coordination induced O-H bond weakening is well documented and we endeavored to experimentally determine the

Scheme 4 PCET thermochemistry of complex H1 .

$\text{BDFE}_{\text{O-H}}$ in H1 using Bordwell's equation (Scheme 4).^{3,6,20,21} Ideally, a pK_a measurement should be carried out in polar solvents like MeCN, DMSO, DMF, water or methanol for which the C_G values in the Bordwell equation are known.²⁰ However, none of these polar coordinating solvents could be used for our pK_a determination. While MeCN generated $\text{H1}+\text{MeCN}$, DMSO, DMA, and DMF led to immediate decomposition to free ligand and other unidentified species, and methanol and water showed poor solubility of H1 . The meta-stable complex H1 is best handled in DCM or chloroform and thus we carried out the pK_a measurements in DCM using freshly prepared compounds. The pK_a of bases in MeCN have been found to be similar to those in DCM, which are taken as identical to those in THF and are linearly correlated (Table 1).^{22–24}

Thus, we treated H1 with various bases in DCM and found that Et_3N ($\text{pK}_{a(\text{MeCN})} = 18.5$) showed no reaction, but one equivalent of DBU ($\text{pK}_{a(\text{MeCN})} = 24.3$) is sufficient to completely convert H1 into a species consistent with $[\text{DBU-H}][\text{1}]$ (Fig. S11b†). $^{31}\text{P}\{^1\text{H}\}$ NMR of the reaction mixture showed a new peak at δ 58.5 ppm (Fig. S11a†) shifted from that of both H1 (δ 54.3 ppm) and $\text{K}[\text{1}]$ (δ 55.2 ppm). The downfield shift of about 3 ppm observed for $[\text{DBU-H}][\text{1}]$ with respect to $\text{K}[\text{1}]$ suggests changes in the primary coordination environment, possibly arising from the replacement of the coordinating metal cation (K^+) with a non-coordinating organic cation ($[\text{DBU-H}]^+$). A similar downfield shift was observed for a reaction between $\text{K}[\text{1}]$ and $[\text{PPN}]\text{Cl}$ generating $[\text{PPN}][\text{1}]$ (Fig. S12†).

Reaction of H1 with Et_3N and DBU narrowed the $\text{pK}_{a(\text{MeCN})}$ range to be within 18.2 to 24.3. Hence, deprotonation of H1 with equimolar TMG ($\text{pK}_{a(\text{MeCN})} = 23.3$) was performed and monitoring the reaction with $^{31}\text{P}\{^1\text{H}\}$ NMR showed two peaks corresponding to H1 ($^{31}\text{P}\{^1\text{H}\}$ NMR δ 54.7 ppm) and $[\text{TMG-H}][\text{1}]$ ($^{31}\text{P}\{^1\text{H}\}$ NMR δ 60.9 ppm) (Fig. S13†) in roughly equimolar amounts. ATR-FTIR of the reaction mixture showed

Table 1 Relevant pK_a values in MeCN and DCM^a

Base	pK_a MeCN ^{24–26}	pK_a THF or DCM ²⁴
DBU	24.3	20
TMG	23.3	17.8
Et ₃ N	18.5	13.7
DMAP	18.2	14.1
Pyridine	12.5	8.3
Aniline	10.6	8
DMF	6.1	1

^a A plot of pK_a in MeCN vs. pK_a in DCM (or THF) gives a straight line with slope = 0.96 and y-intercept = 3.7 ($R^2 = 0.98$).

carbonyl peaks corresponding to **H1** and [TMG-H][1] along with peaks corresponding to **H1**+CO in the baseline from decomposition (Fig. S14†). The reverse reaction by treating [PPN][1] with [TMG-H]BF₄ in CDCl₃ also showed production of **H1**, but with more decomposition to **H1**+CO. The meta-stability of **H1** (even under < 1 ppm O₂) made a precise equilibrium difficult to establish. Therefore, determining K_{eq} was not explicitly possible under the conditions studied here, but it is very close to 1 for the reaction with TMG and **H1**. Hence, the pK_a of **H1** is approximated to be very close to [TMG-H]⁺ (Table 1).^{24,26}

The reduction potential of [1][−] was determined with cyclic voltammetry and was found to be −0.58 V vs. FeCp₂ in MeCN (Fig. 4).²⁷ While there are known examples of meta-stable low-spin Mn(II) dicarbonyl compounds,^{28,29} our limited attempts at isolating the product of [1][−] oxidation (e.g., using FeCp₂⁺ or NO⁺) were unsuccessful despite the reversibility at moderately high scan rates; product of oxidation was mixtures of compounds including **H1**+CO (identified with FTIR) and unidentified paramagnets with EPR signals consistent with high-spin Mn(II) compounds (Fig. S16†).^{13,29} Using the Bordwell

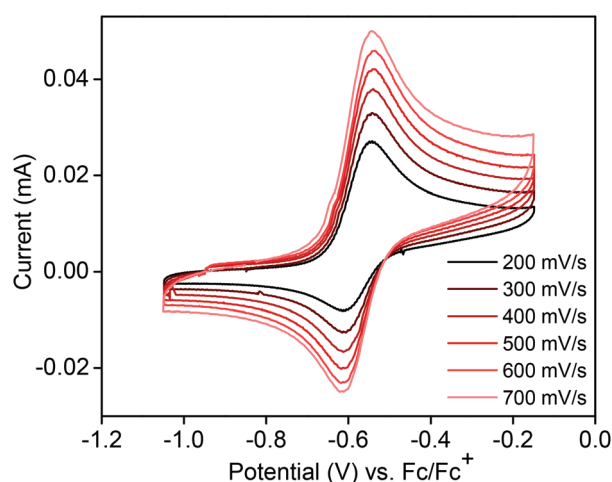


Fig. 4 Cyclic voltammogram of 0.001 M [K1] in MeCN at various scan rates. Experimental conditions: 0.1 M [Bu₄N][PF₆], glassy carbon working electrode, Ag/AgNO₃ reference electrode with a CoralPor™ separator, and platinum auxiliary electrode. $E_{1/2} = -0.58$ V vs. Fc/Fc⁺. Scan direction anodic.

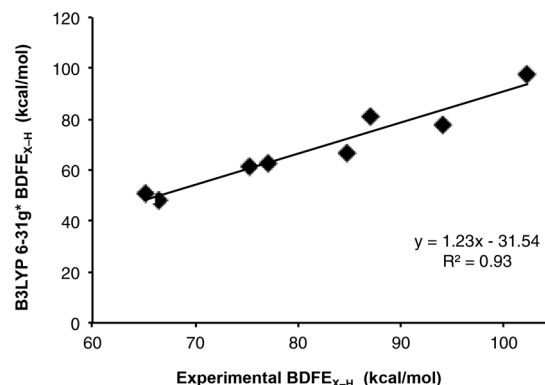


Fig. 5 Computed values of X–H (X = H, C, N, O) bond dissociation energies (BDFE_{X–H}) in kcal mol^{−1} plotted against known experimental values. The points used for this plot are taken from entries 1–8 in Table 2.

equation, it is possible to estimate the MeCN BDFE_{O–H} of **H1** ($pK_a = 23$ and $E_{1/2} = -0.58$ V) to be 73 kcal mol^{−1}.

Since we could not precisely measure the acid/base equilibrium constant for [1][−]/**H1** and used DCM instead of MeCN, we used DFT to support the viability of the estimated MeCN BDFE_{O–H} for **H1**. For this, we computed the BDFE_{X–H} (X = H, C, N, O) of several compounds for which the BDFE_{X–H} is known and plotted the computed values vs. known experimental values (Fig. 5).²⁰ This approach gives a straight line with which we can estimate a “corrected BDFE_{O–H}” for the complexes **H1**, **H1'**, and **H1**+CO (Scheme 4).³⁰ The uncorrected computed values were found to be 51.4 kcal mol^{−1} for **H1**, 54.3 kcal mol^{−1} for the H-bonded isomer of **H1**,¹³ 62.1 kcal mol^{−1} for **H1'**, and 77.1 kcal mol^{−1} for **H1**+CO, which when corrected are 68.0, 70.3, 76.7, and 89.0 kcal mol^{−1} for **H1**, H-bonded isomer of **H1**, **H1'**, and **H1**+CO, respectively (Scheme 4).

Table 2 Computed and experimental BDFE_{X–H} in MeCN^a

Entry	Compound	DFT ^b	BDFE _{X–H} (kcal mol ^{−1})	
			Experimental ^c	Corrected
1	TEMPO–H	47.9	66.5	65.1
2	dtbuHA	51.4	65.2	68.0
3	TOC	61.7	75.2	76.4
4	2,4,6-ttbp	64.1	77.1	78.3
5	NHPI	65.5	84.8	79.5
6	Aniline	79.6	94.1	91.0
7	Toluene	81.7	87	92.7
8	H ₂	92.08	102.3	101.2
—	H1 +CO	77.1	—	89.0
—	H1'	62.1	—	76.7
—	H1 (w/H-bond)	54.3	73	70.3
—	H1 (no H-bond)	51.4	—	68.0

dtbuHA = *N,N*-di-*tert*-butylhydroxylamine; TOC = Trolox C; 2,4,6-ttbp = 2,4,6-tritertbutylphenol; NHPI = *N*-hydroxyphthalimide. ^a BDFE values are in kcal mol^{−1}, standard conditions. ^b B3LYP 6-31G* with SMD solvation model for MeCN. ^c Experimental BDFE_{O–H} from ref 20.

Conclusions

We have characterized the first example of a low-spin d^6 first-row transition metal complex containing a M–O linkage where the O-atom is from a phenol (M–Ph(O)H), namely in [(HPO)(PO)Mn(CO)₂] (**H1**). Complexes like **H1** are rare because coordination of a phenolic O-atom destabilizes the O–H bond toward homolysis. This hypothesis was tested through a thermochemical analysis of the O–H bond strength in **H1** and observing its general chemical and physical properties. For instance, crystals of **H1** suitable for diffraction were only attainable for the deuterated species. The structure reveals that **H1** contains the first Mn(I)–O linkage where the O-atom is phenolic. The phenolic ligand is hemilabile, which was determined through DFT and its reactivity with MeCN ([**1**][−] and **H1**+CO do not react with MeCN). Compound **H1** exhibited the hallmarks of homolytic instability, spontaneously decomposing into a mixture of species containing both **H1**+CO and Mn^{II}[**1**]₂, the latter of which is believed to have formed through decomposition initiated by a PCET reaction with **H1**. Some of the known d^6 2nd and 3rd row-transition M–Ph(O)H complexes exhibit similar thermal instability, and our work provides the first thermochemical analysis to provide one possible explanation. The decomposition of **H1** is accelerated by addition of TEMPO or small amounts of air, the former of which converts into TEMPOH. Of the isomers computed for **H1**, the lowest energy isomer contains an intramolecular H-bond. This isomer has a corrected calculated BDFE_{O–H} of 70.3 kcal mol^{−1} and supports the estimated experimental value of 73 kcal mol^{−1}, which was obtained using Bordwell's equation in MeCN. We pursued the DFT analysis because we were unable to make precise pK_a measurements in DCM or in MeCN. The computed value for the 16-e[−] isomer **H1'** (corrected DFT value = 76.7 kcal mol^{−1}), which essentially has a free tri-substituted phenol, is close to that of 2,4,6-tritertbutylphenol (experimental value = 77.1 kcal mol^{−1}). Therefore, it is apparent how the coordination event lowers the BDFE_{O–H}. The higher value for **H1**+CO (computed 89.0 kcal mol^{−1}) is consistent with energy gained from the intramolecular O–H...O hydrogen bonding interaction. These data support the key hypothesis in soft-homolysis of coordination induced X–H bond weakening, a paradigm that has emerging utility in energy science and chemical synthesis.

Experimental section

General methods

All reagents were procured from commercial sources and were used without further purification unless otherwise noted. Solvents were purified and collected from a PPT solvent system and stored over 3 Å molecular sieves. Molecular sieves and basic alumina were activated at 200 °C under vacuum (<100 mTorr) for 48 hours before use. Unless noted, all the samples were prepared under nitrogen in a VAC Genesis glove box or under argon using standard Schlenk line techniques. Deuterated solvents were degassed by freeze–pump–thaw

method and stored in the glove box in Strauss flasks. NMR experiments were performed on Varian Mercury-300 MHz, Inova-400 MHz, and Inova-500 MHz spectrometers. Transmission and ATR-FTIR spectra were collected inside of a VAC Atmospheres Omni glovebox using a Bruker Alpha IR spectrometer with ALPHA-P Platinum ATR module (diamond crystal). Cyclic voltammetry was obtained using a SP-200 Bio-Logic potentiostat. Headspace analysis was obtained using a PerkinElmer Clarus 580 GC (thermal conductivity detector, Ar carrier gas). EPR spectra were collected on a EMX Bruker X-band spectrometer on frozen solutions at 77 K. UV–vis spectra were collected using an 8154 Agilent Spectrophotometer. High resolution mass spectroscopy was performed in MeCN using an FT ICR Bruker 12 T mass spectrometer. Deuterated lutidinium tetrafluoroborate ([Lt-D]BF₄) was prepared by stirring [Lt-H]BF₄ in *d*₄-methanol for 12 h and removing the volatiles under vacuum. Compounds HPO, K[**1**], **H1**+CO and Mn^{II}[**1**]₂ were prepared according to previous literature.¹³

Computational methods

All DFT calculations were performed using QChem 4.4,³¹ and used the B3LYP functional, 6-31G* basis set, and SMD solvation model for MeCN and toluene. Geometry optimizations were performed using the crystal coordinates or manipulated/inputted in IQmol directly. Frequency calculations were performed on all structures to ensure no imaginary frequencies. Single point energy calculations were used to obtain the final electronic energy (enthalpy).

Synthesis of (HPO)(PO)Mn(CO)₂ (**H1**)

A solution of K[**1**]·(THF)₃ (90 mg, 0.09 mmol, 1.0 eq.) in DCM (2 mL) was cooled to −35 °C. A cold solution of [Lt-H]BF₄ (19 mg, 0.10 mmol, 1.1 eq.) in DCM (1 mL) was added dropwise. The solution immediately turned deep orange with the formation of white ppt. The reaction was allowed to stir for 1 h at rt. The solution was filtered using a fine frit and the ppt was washed with DCM. Removing the solvent from the red filtrate under vacuum yielded orange solid residue, which was washed with petroleum ether to remove the lutidine left behind. This orange solid was dried under vacuum to yield **H1** (64 mg, 95% yield). ¹H-NMR (*d*₂-DCM, 300 MHz, 298 K, ppm): δ 1.43 (s, 6H, CH₃), 2.16 (s, 6H, CH₃), 2.69 (s, 1H, OH), 3.71 (s, 4H, CH₂), 6.69 (s, 2H, CH), 6.72 (s, 2H, CH), 7.3–7.7 (20H, (C₆H₅)₂P). ³¹P{¹H} NMR (*d*₂-DCM, 121 MHz, 298 K, ppm): δ 54.3 ppm. FTIR-ATR (cm^{−1}): 3480, 1923, 1844.

The deuterated compound *d*₁-**H1** was synthesized following the above-mentioned procedure using [Lt-D]BF₄. Crystals suitable for XRD was obtained by layering a solution of *d*₁-**H1** in DCM under petroleum ether.¹⁴

Synthesis of (HPO)(PO)Mn(CO)₂(MeCN) (**H1** + MeCN)

The acetonitrile bound complex (**H1**+MeCN) was prepared using the following procedure. A solution of K[**1**]·(THF)₃ (90 mg, 0.09 mmol, 1.0 eq.) in MeCN (2 mL) was cooled to −35 °C. [Lt-H]BF₄ (19 mg, 0.10 mmol, 1.1 eq.) in MeCN was

added while cold, during which the color changed from orange to yellow immediately along with precipitate formation. The reaction was allowed to stir at rt for 1 h. The solution was filtered using a glass fritted funnel and the precipitate collected. The precipitate was washed with MeCN. DCM was added to the material in the fritted funnel and filtered to collect a yellow filtrate, leaving behind a white residue. Removing volatiles from the filtrate under vacuum yielded **H1**+MeCN as yellow solid (65 mg, 92% yield). The DCM filtrate when layered under hexane and stored at $-35\text{ }^{\circ}\text{C}$ for one week yielded yellow crystals suitable for XRD. The compound **H1**+MeCN is either insoluble or sparingly soluble in common organic solvents like MeCN, THF, diethyl ether, benzene, toluene, acetone and methanol. Even though the compound tends to degrade in chlorinated solvents, its limited solubility in only DCM or chloroform required their use. ^1H NMR in chlorinated solvents led to broad peaks and inconclusive NMR data due to the presence of paramagnetic impurities arising from degradation.¹⁴ $^{31}\text{P}\{^1\text{H}\}$ NMR (DCM, 121 MHz, 298 K, ppm): δ 78.5, 64.9 ppm. FTIR-ATR (cm^{-1}): 2330, 1941, 1862.

Elemental composition of **H1** and **H1** + MeCN

Due to the instability of compound **H1** and **H1**+MeCN, CHN combustion analysis was not performed. Instead, HR-MS data were collected for a solution of **H1**+MeCN in MeCN prepared freshly from K[1], which showed the presence of **H1**+H⁺ and **H1**+MeCN+H⁺. Major peak; $[\text{M-MeCN} + \text{H}]^+ [\text{C}_{44}\text{H}_{42}\text{MnO}_4\text{P}_2]^+ m/z(\text{found}) = 751.19625; m/z(\text{calculated}) = 751.19333$. Minor peak; $[\text{M} + \text{H}]^+ [\text{C}_{46}\text{H}_{45}\text{MnNO}_4\text{P}_2]^+ m/z(\text{found}) = 792.22293; m/z(\text{calculated}) = 792.21988$.

pK_a estimation of **H1**

A solution of **H1** (10 mg, 0.01 mmol, 1.0 eq.) in DCM was treated with 1.0 eq. of base and the reaction was monitored using $^{31}\text{P}\{^1\text{H}\}$ NMR (ESI figures†).

In situ synthesis of (Me₃SiOP)(PO)Mn(CO)₂ (**Me³Si1**)

A solution of K[1] (15 mg, 0.02 mmol, 1.0 eq.) in ether (2 mL) was cooled to $-78\text{ }^{\circ}\text{C}$. Me₃SiOTf (2.5 μL , 1.0 eq.) was added using a syringe. The color immediately turned deep red. The reaction was allowed to warm to rt overnight. The reaction mixture was filtered and the filtrate collected. $^{31}\text{P}\{^1\text{H}\}$ NMR (hexane, 121 MHz, 298 K, ppm): δ 51.7, 51.9 ppm. FTIR-ATR (cm^{-1}): 1925, 1851. This compound is thermally unstable and was not characterized further.

Conflicts of interest

The authors declare no competing financial interests.

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