Metallocenophanes

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Strained Metallocenophanes with Late Transition Metals in the Bridge: Syntheses and Structures of Nickel- and Platinum-Bridged [1]Ferrocenophanes

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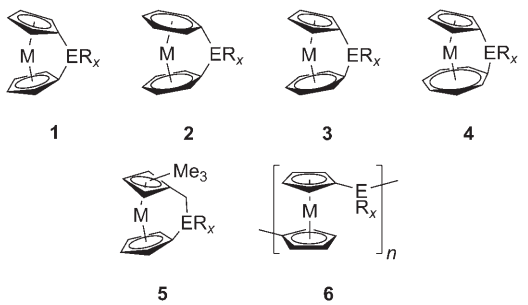
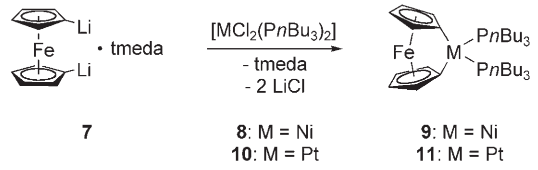
Until recently, few classes of strained rings containing transition elements had been explored, but these interesting species are now attracting substantial attention.[1] In particular, strained metallocenophanes (**1**) and related species



containing π-hydrocarbon ligands (e.g. **2**–**5**)[2] have been the focus of recent investigations due to the fascinating questions that surround their electronic structures, bonding, and reactivity. Furthermore, the ability of these compounds to yield functional metallopolymers by ring-opening polymerisation (ROP) has provided an extra impetus to the field.[3] The nature of the transannular bridge, ER$_x$, in such species is of pivotal importance as the size and geometric preferences of the bridging element directly influence the strain present. Moreover, in the ring-opened polymers **6** the metal–metal interactions are modulated by the spacer unit.[4] To date, most work in the area of strained metallorings has involved [1]ferrocenophanes (e.g. **1**, M = Fe) containing bridging non-metallic main group elements E such as Si, P, and more recently S and B.[2a] The incorporation of main group metals (Sn,[5] Al,[2c,6] and Ga[2c,7]) and early d-block metals (Ti, Zr, and Hf)[8] has also been successful. However, to date no transition metals other than the aforementioned Group 4 d^0 tetrahedral centers have been successfully introduced into the bridge. Herein, we report examples of [1]ferrocenophanes with the Group 10 metals Ni and Pt in the bridge, which leads to strained, unexpectedly electron-rich species containing square-planar d^8 centers.

The scarcity of metal-bridged [1]ferrocenophanes is at first sight somewhat surprising, given that the main synthetic route to these molecules would appear applicable to any element for which a dichloride is available.[2a] We have found, however, that reaction of many transition-metal dihalides with dilithioferrocene–tmeda complex (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) results in reduction of the metal center. For instance, treatment of $Li_2[Fe(\eta^5\text{-}C_5H_4)_2]\cdot$tmeda (**7**)[9] with *trans*-$[NiCl_2(PMe_3)_2]$,[10] in hexane at −20 °C, only leads to the precipitation of metallic nickel. In striking contrast, the analogous reaction of **7** with *trans*-$[NiCl_2(PnBu_3)_2]$ (**8**, Scheme 1)[11] resulted in a cloudy, dark red solution with a single new product detected by $^{31}P\{^1H\}$ NMR spectroscopy ($\delta = 13.5$ ppm, ca. 20 % conversion). Work-up afforded a dark red crystalline solid in modest yield (11 %) that was subsequently characterized as the first nickel-bridged [1]ferrocenophane $[\{Fe(\eta^5\text{-}C_5H_4)_2\}Ni(PnBu_3)_2]$ (**9**).[12] It is of interest that the Ni^{II} component readily undergoes a *trans*-to-*cis* isomerisation during the reaction and that no product containing the original *trans* configuration was observed.



Scheme 1. Preparation of metal-bridged [*n*]ferrocenophanes.

Compound **9** was fully characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. It is noteworthy that all three spectra displayed resonances at predictable chemical shifts and as such were consistent with the incorporation of a diamagnetic square-planar nickel(II) center. The ^1H NMR spectrum of **9** is typical of [1]ferrocenophanes with the two sets of cyclopentadienyl protons experiencing markedly different shielding ($\Delta\delta = 0.3$ ppm).[2a] Further indication of the strained nature of **9** can be taken from the $^{13}C\{^1H\}$ NMR spectrum. The *ipso*-carbon resonance of the carbocyclic rings ($\delta = 54.1$ ppm) appears at higher field than the signal observed for ferrocene ($\delta = 69$ ppm).[13] This is attributed to an increase in sp^3 character of the *ipso*-carbons, which results from a strain-induced distortion of these atoms away from the initial trigonal-planar geometry. For the only other transition-

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metal-bridged [1]ferrocenophanes to have been prepared, the reverse effect was reported with [{Fe(η^5-C_5H_4)$_2$}M(η^5-C_5H_4tBu)$_2$] (M = Ti, Zr and Hf) exhibiting ^{13}C{^{1}H} resonances at $\delta = 179.8$, 159.0, and 153.3 ppm, respectively.[8] The solid-state structure of the sole crystallographically characterized example (M = Zr), however, suggested that these were only modestly strained ($\alpha = 6°$). The lowest-energy electronic transition of ferrocene (440 nm)[14] has been shown to be sensitive to the degree of ring-tilt and the formation of [1]ferrocenophanes is classically accompanied by a bathochromic shift of this band.[2a] The UV/Vis spectrum of **9** exhibited a corresponding transition at 478 nm and thus is consistent with the formation of a [1]ferrocenophane. Unfortunately, no molecular ion peak was observed when **9** was subjected to EI-MS.

To investigate the generality of the synthetic procedure, *cis*-[PtCl$_2$(PnBu$_3$)$_2$][15] (**10**) was treated with **7**. This experiment also afforded a metal-bridged [1]ferrocenophane, namely [{Fe(η^5-C_5H_4)$_2$}Pt(PnBu$_3$)$_2$] (**11**), although in this instance the availability of a *cis*-dichloride precluded the need for isomerisation at the bridging metal center. It therefore appears that formation of a [1]ferrocenophane is not exclusive to nickel but can be extended to platinum. The NMR and UV/Vis spectroscopic data for **11** does not differ significantly from that for **9** and therefore will not be discussed further. The observation of a platinum–phosphorus coupling constant [^1J(Pt,P) = 2182 Hz], however, is noteworthy as it is consistent with the presence of a square-planar Pt^{II} center.[16]

Both compounds **9** and **11** were characterized by single crystal X-ray diffraction (see Figure 1 for **9**) and all pertinent structural parameters are included in Table 1.[17] Upon cooling concentrated hexane solutions to −40°C, the compounds crystallized as red blocks in the monoclinic space group $P2_1/c$. The crystals were isomorphous and contained one molecule per asymmetric unit with no short intermolecular interactions. By virtue of the constraining *ansa*-bridge, the Cp ligands subtended an angle (α) of 28.4° and 25.2° in **9** and **11**, respectively. As would be expected given the increased covalent radius[18] of platinum (1.29 Å) with respect to nickel (1.15 Å), compound **11** exhibits the lower α angle in the solid state. It is noteworthy that both **9** and **11** possess higher tilts than the only other crystallographically characterized [1]ferrocenophane to contain a transition metal in the bridge, [{Fe(η^5-C_5H_4)$_2$}Zr(η^5-C_5H_4tBu)$_2$] ($\alpha = 6°$).[8] This clearly arises from a combination of the more constraining square-planar geometries of the Group 10 metals and the contraction in covalent radius that occurs on traversing a period of the d-block. The Fe–Cp(centroid) distances (1.62–1.64 Å) are comparable to those found in the sila[1]ferrocenophane, [Fe(η^5-C_5H_4)$_2$SiMe$_2$] (**1**: M = Fe, ER$_x$ = SiMe$_2$) (both 1.63 Å).[19] This parameter, however, has been shown to be relatively insensitive to the strength of Fe−Cp bonding. In cases where the Cp rings are more firmly bound, deformation occurs preferentially at the Cp *ipso*-carbon atoms.[20] This is due to the higher energy penalty associated with tilting the Cp rings and is manifested structurally in higher β and lower α angles. In **9** and **11** the converse is true, with the β angles proving considerably less marked (25.5 and 25.9° for **9**, and 26.4 and 26.2° for **11**) than in **1** (M = Fe, ER$_x$ = SiMe$_2$) [both 37.0(6)°].[19] It would therefore appear that Fe−Cp bonding is in fact weaker in the former compounds. The geometry about the nickel and platinum centers is best described as distorted square-planar with *cis* phosphine ligands. It is noteworthy that these represent the first ferrocenophanes to contain an element with a square-planar geometry in the *ansa*-bridge. The angle subtended by the two Ni−C(*ipso*) bonds (θ) [80.7(2)°] is smaller than the ideal angle (90°). When taken together, these observations suggest that it is distortion of the iron coordination environment, and not the *ipso*-carbons or Group 10 center, that mainly accommodates the strain of the system.

Table 1: Summary of pertinent structural data for metal-bridged [1]ferrocenophanes **9** and **11**.

Parameter	M = Ni (**9**)	M = Pt (**11**)
α [°]	28.4	25.2
β [°]	25.5	26.4
	25.9	26.2
δ [°]	157.3	159.4
θ [°]	80.7(2)	78.36(16)
Fe–Cp(centroid) [Å]	1.62	1.64
		1.63
Fe⋯M [Å]	3.03	3.14

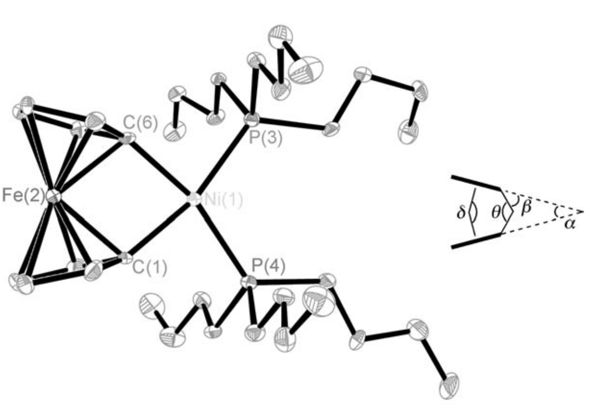

Figure 1. Left: Molecular structure of **9** as determined by single crystal X-ray diffraction (thermal ellipsoids are set at 50% probability). All hydrogen atoms have been omitted for clarity. Right: Definition of parameters used to quantify distortion in [1]ferrocenophanes.

Compounds **9** and **11** were subjected to a cyclic voltammetric study in order to probe any electronic effect that the bis(phosphine)metal(II) fragments may have on the ferrocene/ferrocenium redox couple. The platinum-containing compound **11** exhibited an electrochemically reversible redox couple, as was previously reported for sila[1]-,[20] germa[1]-,[21] and stanna[1]ferrocenophanes,[5c] whereas oxidation proved irreversible in the case of **9**. The most striking feature of each voltammogram was the oxidation potential, which occurred at −0.821 (E_p) and −0.682 V ($E°$) versus the ferrocene/ferrocenium redox couple (scan rate of 250 mV s^{-1}) for compounds **9** and **11**, respectively. Despite an appreciable tilt angle [20.8(5)°],[19] the half-wave oxidation potential for **1** (M = Fe, ER$_x$ = SiMe$_2$) is identical to that of ferrocene and, thus, it would appear that this property is insensitive to distortion of the ferrocenediyl group. Cathodic shifts have, however, been observed upon increased methylation of the Cp rings,[20] but these have always been attributed to an increase in electron-density at the iron center. Furthermore, such changes have been correlated with decreasing α and increasing β angles, whereas analysis of the solid-state structures here shows the converse to be true. It is conceivable that a dative interaction from the bis(phosphine)metal(II) fragment to the iron center may stabilize the resulting iron(III) complex relative to the ferrocenium ion, which could lead to the observed shift in the redox potential. The spatial separation between the two metal centers in each compound (Table 1), however, is at least 27 % larger than the sum of the covalent radii. It is noteworthy that in **1** ($M = Fe$, $ER_x = SiMe_2$) the $Fe\cdots Si$ interaction is also larger than the sum of covalent radii (by 18 %), although the ^{57}Fe Mössbauer spectrum suggested a possible dative interaction between silicon and iron.[20] This feature, however, did not result in the expected anodic shift of the oxidation potential and thus it difficult to invoke such an argument for the marked change in $E°$ for **11** given the larger effective interatomic separation.

From the X-ray data, the two new metal-bridged [1]ferrocenophanes **9** and **11** appear to be highly strained species that should undergo ring-opening reactions. In the initial studies, given that the large α angle suggested a weakening of the Fe–Cp bonds, we explored the use of NaCp-initiated photolytic ROP.[22] This process proceeds through the cleavage of Fe–Cp bonds, and as such differs from the "dark" variation, initiated with alkyl or aryl lithiums, where the bridging atom–Cp bond is broken.[23] However, under the same conditions that proved successful for the photolytic ROP or stoichiometric ring-opening of **1** ($M = Fe$, $ER_x = SiMe_2$), compound **11** remained unchanged as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. Further attempts to ring-open **11** by reaction with PhLi and *n*BuLi also resulted in no reaction, even when **11** was stirred at 25 °C with 10 equivalents of *n*BuLi for 18 h. We investigated whether compound **11** could be ring-opened thermally. After heating in the melt at 150 °C for 18 h, $^{31}P\{^1H\}$ NMR spectroscopy indicated that the starting material was completely unchanged. Further heating at 210 °C for 12 h, however, resulted in a brown solid forming from the red melt. Analysis of this material by $^{31}P\{^1H\}$ NMR spectroscopy revealed dissociated $PnBu_3$ to be the only phosphorus-containing component.

In conclusion, the application of the $PnBu_3$ ligand has enabled the synthesis and characterization of the novel d^8 metal-bridged [1]ferrocenophanes, **9** and **11**, which display substantial structural differences from early d^0 transition-metal analogues and unexpected redox properties. Compound **11** decomposed through phosphine dissociation prior to undergoing any well-defined ring-opening chemistry. We are currently investigating the use of stronger donors such as bidentate diphosphines to circumvent the problems associated with ligand loss and prepare mixed-metal polymetallocenes by ROP.

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[17] Crystal structure data for **9**: red blocks from hexane; $C_{34}H_{62}FeNiP_2$, monoclinic, space group $P2_1/c$; $a = 18.170(4)$, $b = 9.5255(19)$, $c = 20.973(4)$ Å, $\alpha = 90$, $\beta = 107.40(3)$, $\gamma = 90°$, $V = 3463.9(12)$ Å^3; $Z = 4$, $\rho_{calcd} = 1.241$ g cm^{-3}; crystal dimensions: $0.2 \times 0.1 \times 0.05$ mm; diffractometer: Bruker Smart Apex CCD; $Mo_{K\alpha}$ radiation, 100(2) K, $2\theta_{max} = 55.96°$; 38899 reflections, 7936 unique ($R_{int} = 0.1421$), direct methods; absorption correction SADABS ($\mu = 1.075$ mm^{-1}); refinement (against F_o^2) with SHELXTL-97, 349 parameters, 0 restraints, $R_1 = 0.0827$ ($I > 2\sigma$) and $wR_2 = 0.1693$ (all data), Goof = 1.143, max/min residual electron density: 0.589/−1.013 e Å^{-3}. Crystal structure data for **11**: red blocks from hexane; $C_{34}H_{62}FeP_2Pt$, monoclinic, space group $P2_1/c$; $a = 18.301(4)$, $b = 9.6527(19)$, $c = 20.902(4)$ Å, $\alpha = 90$, $\beta = 107.77(3)$, $\gamma = 90°$, $V = 3516.4(12)$ Å^3; $Z = 4$, $\rho_{calcd} = 1.480$ g cm^{-3}; crystal dimensions: $0.3 \times 0.1 \times 0.05$ mm; diffractometer: Bruker Smart Apex CCD; $Mo_{K\alpha}$ radiation, 100(2) K, $2\theta_{max} = 100.630°$; 39427 reflections, 8073 unique ($R_{int} = 0.0673$), direct methods; absorption correction SADABS ($\mu = 4.498$ mm^{-1}); refinement (against F_o^2) with SHELXTL-97, 349 parameters, 0 restraints, $R_1 = 0.0382$ ($I > 2\sigma$) and $wR_2 = 0.0772$ (all data), Goof = 1.080, max/min residual electron density: 1.397/−1.692 e Å^{-3}. CCDC 670448 (**9**) and CCDC 670449 (**11**) 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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