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Bridging Vinyliminium- and Enaminoalkylidenediiron Complexes as Organometallic Ligands

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The SPh-functionalized vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')=C_\beta(SPh)C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Xyl, R′ = Me, **3a**; R = R′ = Me, **3b**; R = Xyl, R′ = CH_2OH, **3c**; R = Me, R′ = CH_2OH, **3d**; Xyl = 2,6-$Me_2C_6H_3$; Cp = $\eta^5C_5H_5$) react with $NaBH_4$, in thf solution, to afford the corresponding μ-vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')\text{-}C_\beta(SPh)=C_\alpha(H)N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**5a–d**). This reaction transforms the iminium into an amine group, thereby generating an N-donor functionality. Consequently, the bridging organic framework in **5a–d**, which contains S and N donor atoms, can act as an ambidentate ligand toward coordinatively unsaturated metal fragments. In particular, the complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')C_\beta(SPh)=C_\alpha(H)NMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = Me, **5b**; R′ = CH_2OH, **5d**) react with $[PdCl_2(CH_3CN)_2]$ to give $[PdCl_2$(N,S-**5b**)] (**6a**) and $[PdCl_2$(N,S-**5d**)] (**6b**), respectively. The molecular structure of **6b** has been determined by X-ray diffractometry. In an analogous reaction, compound **5d** acts as an "organometallic ligand" for the unsaturated rhodium fragment generated upon treatment of $[Rh(NBD)Cl]_2$ (NBD = norbornadiene) with $AgClO_4$. This reaction affords the trinuclear complex [Rh(NBD)(κ^2-N,S-**5d**)][ClO_4] (**7**). The bridging ligand in the zwitterionic complex $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(CH_2OH)=C_\beta(S)C_\alpha=N\text{-}(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2a**) contains an OH group in addition to the N and S functionalities. This bridging framework acts as a O,S bidentate ligand and the reaction of **2a** with $[Ti(Cp)_2(CH_3CN)_2](SO_3CF_3)_2$ leads to the formation of the adduct $[Ti(Cp)_2$(κ^2-O,S-**2a**)]$[SO_3CF_3]_2$ (**8**).

Introduction

Organometallic complexes in which the ligands contain donor heteroatoms like P, N, O, or S not directly involved in coordination are potentially able to exploit these functionalities to coordinate further (external) metal centers. These organometallic species might therefore act as "organometallic ligands" and produce the assembly of more complex molecular architectures.[1] This idea is not new,[2] but only recently has the use of organometallic species as ligands become more extensive. Perhaps the most important example involves ferrocenyl ligands,[3] which have experienced an impressive growth due to their applications in the field of asymmetric catalysis.[4] This extraordinary development is related to the versatility of ferrocenyl ligands themselves, which can be electronically and/or sterically designed more easily than other traditional ligands in order to affect the environment around the catalytically active metal center.

Beside the use of ferrocenes in catalysis, other applications of "organometallic ligands" can be envisaged in the field of molecular assembly. This concept is analogous to that of "expanded ligands", which incorporate metal-containing groups as spacers between metal-binding domains.[5] Examples include novel classes of supramolecular coordination assemblies with organometallic linkers[6] and the construction of potential molecular motors based on functionalized organometallic species as building blocks.[7]

Our interest in the field of organometallic complexes containing highly functionalized ligands has been focused on the chemistry of bridging vinyliminiumdiiron complexes **1**[8] and on the transformations which can be performed on the bridging ligand (Scheme 1). These include functionalization with sulfur and thiolates (Scheme 1, complexes **2**[9] and **3**[10]). In particular, zwitterionic complexes of type **2** contain an S functionality which is potentially able to coordinate unsaturated metal fragments, as evidenced by coordination of the Fp^+ group [Fp = $Fe(CO)_2Cp$][11] to form the trinuclear compound **4** (Scheme 1).

A more effective use of these dinuclear complexes as "organometallic ligands" should exploit the presence of both heteroatoms (N and S) in the bridging framework in order to render the ligand chelating with respect to an external (additional) metal centre. However, this is not possible in complexes of type **2** or **3** due to the iminium nature of the group, which does not leave any residual donor ability on the N atom.

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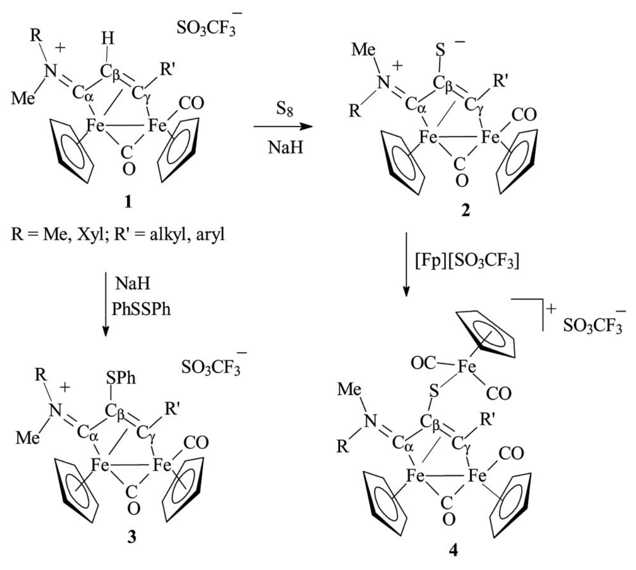


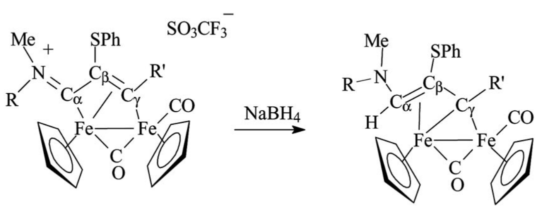
Scheme 1.

The present work concerns the modifications performed on the bridging framework in order to transform the iminium group into an effective N donor and confer the properties of a chelating ligand on this framework. Investigations on the effectiveness of these "organometallic ligands" with respect to the coordination of various transition metals are reported.

Result and Discussion

Synthesis of Chelating Organometallic Ligands

Transformation of the bridging vinyliminium ligand into a chelating framework which is potentially able to coordinate further metal centers has been pursued through conversion of the iminium group into an effective N donor functionality. This goal has been accomplished by treating the vinyliminium complexes **3a**–**d**, which contain an SPh group, with NaBH$_4$ (Scheme 2). Hydride addition occurs at the iminium carbon (C$_\alpha$) and transforms the vinyliminium complexes into the corresponding enaminoalkylidene complexes **5a**–**d**.



	R	R'	
3a	Xyl (Xyl = 2,6 Me$_2$C$_6$H$_3$)	Me	**5a**
3b	Me	Me	**5b**
3c	Xyl	CH$_2$OH	**5c**
3d	Me	CH$_2$OH	**5d**

Scheme 2.

Nucleophilic addition of hydride (from NaBH$_4$) to the C$_\alpha$ atom in bridging vinyliminium complexes has been described previously,[12] therefore the results reported in Scheme 2 were reasonably predictable, although in a number of cases hydride addition has been observed to occur at C$_\beta$ instead of C$_\alpha$. It was previously shown that steric arguments largely determine the site of attack: a sterically demanding Xyl group as N-substituent makes the iminium carbon less accessible to the incoming nucleophile and directs the hydride attack to the adjacent C$_\beta$. Conversely, sterically demanding substituents at C$_\beta$ favor the attack at the iminium group.[12b] For this reason, we examined a few complexes with different substituents (R and R′), in order to determine which among the steric effects was predominant. Since we exclusively observed hydride addition at the iminium carbon, and complexes **5a**–**d** were obtained in good yield from the readily available type **3** complexes, this synthetic approach proved to be very effective in producing N,S-chelating organometallic ligands.

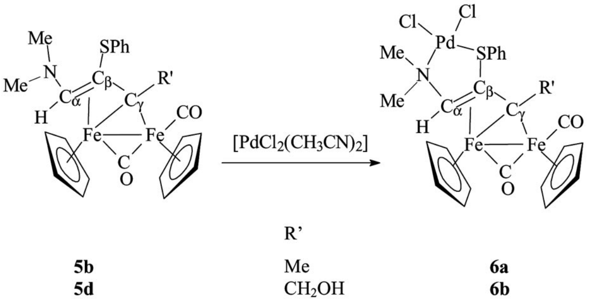
Complexes **5a**–**d** were purified by chromatography on alumina and characterized by spectroscopy and elemental analysis. The spectroscopic properties of **5a**–**d** closely resemble those of analogous enaminoalkylidene complexes reported previously.[12] The IR spectra exhibit the usual ν_{CO} band pattern consisting of two absorptions due to the terminal and bridging CO groups (e.g. at 1929 and 1753 cm^{-1} for **6a**), which are shifted by about 60 cm^{-1} to lower frequencies compared to those of the parent cationic complexes.

The NMR spectra (CDCl$_3$ solution) show the presence of a single isomer, thus indicating that hydride addition is regio- and stereospecific. The upfield-shifted resonance assigned to the C$_\alpha$H (e.g. at δ = 0.98 ppm for **5a**) is consistent with the corresponding values in analogous enaminoalkylidene complexes reported previously.[12] These similarities indicate that **5a**–**d** adopt the same geometry, with the NMe(R) group pointing far from the metal centre and C$_\alpha$–H "*trans*" with respect to the SPh group. The two N-bonded methyl groups in compounds **5b** and **5d** give rise to a single signal. This equivalence is due to fast rotation around the C$_\alpha$–N bond (on the NMR timescale) at room temperature, thus indicating that there is no π-interaction between the two atoms and that the NMe$_2$ group has an amine character.

The ^{13}C NMR spectra of **5a**–**d** show resonances attributable to the C$_\alpha$, C$_\beta$, and C$_\gamma$ carbons in the expected range (e.g. at δ = 107.5, 68.9, and 190.9 ppm, respectively, for **5a**). In particular, the C$_\gamma$ resonance appears downfield shifted, in agreement with its μ-alkylidene character.

Coordination of the Organometallic Complexes to Pd^{II}, Rh^{I}, and Ti^{IV}

Transformation of the iminium moiety into an enamine makes the N(Me)R group available for metal coordination. The bridging frameworks in complexes **5** display N and S functionalities, thus making them potentially able to act as ambidentate ligands. It should be noted that the combination of chemically diverse donor fragments is of particular interest in that is expected to influence the reactivity properties of the associated metal fragment in a way different to that produced by chelating ligands with identical donor groups.[13] Among the number of different transition metal elements which should be coordinated by the N and S atoms of the complex **5**, we initially investigated palladium in light of the increasing interest in Pd complexes containing chelating ligands based on N, S donor atoms.[14] Indeed, Pd complexes containing heterodifunctional bidentate ligands that present hard (N) and soft (S) donors have shown interesting applications in the field of homogeneous catalysis,[15] medicinal chemistry,[16] and mesomorphic materials.[17] We found that compounds **5b** and **5d** react with [$PdCl_2(CH_3CN)_2$], in CH_2Cl_2 solution at room temperature, to give the trinuclear species [$PdCl_2$(κ^2-N,S-**5b**)] (**6a**) and [$PdCl_2$(κ^2-N,S-**5d**)] (**6b**), respectively (Scheme 3).



Scheme 3.

Complexes **6a**,**b** have been characterized by IR and NMR spectroscopy and elemental analysis. Moreover, the molecular structure of **6b**·CH_3CN has been determined by X-ray diffraction studies (Figure 1 and Table 1). The molecular structure of **6b** can be viewed as the result of S,N-coordination of a *cis*-$PdCl_2$ fragment to the enaminoalkylidene compound **5d**. The bonding parameters of **6b** are compared in Table 1 with structurally characterized enaminoalkylidene complexes such as [Fe_2{μ-η^1:η^3-C(Tol)CH=CHNMe$_2$}(μ-CO)(CO)(Cp)$_2$] (**I**)[12a] and [Fe_2{μ-η^1:η^3-C(Me)C(Me)=CHN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$] (**II**).[18] The coordination around the Pd center is perfectly square-planar, with a mean deviation from the least-squares plane of 0.0333 Å and a sum of the angles at Pd(1) of 360.0(3)°. The main result of Pd coordination to the S and N functionalities of the enaminoalkylidene fragment is that N(1) completely loses its planarity and becomes sp^3-hybridized [average C–N(1)–C angles are about 107°] and C(15)–N(1) is considerably elongated, as expected for a pure single bond [1.490(9) Å in **6b**, compared with 1.375(8) and 1.398(3) Å in **I** and **II**]. Moreover, the C(13)–C(14) [1.430(10) Å] and C(14)–C(15) [1.430(10) Å] interactions become identical within experimental error, thus suggesting an allyl-like coordination to the iron centers.

The spectroscopic data are consistent with the structure found in the solid state. In particular, the NMR spectra (acetone solution) show only one set of resonances, thus indicating the presence of a single isomer in solution which, presumably, adopts the same conformation observed in the solid state. The coordination of Pd^{II} does not modify the structure of the C_3 bridging ligand significantly as it exhibits ^{13}C NMR resonances in the usual range (e.g. for **6a** at δ = 94.9, 85.2, and 191.8 ppm for C_α, C_β, and C_γ, respectively). In contrast to the parent complexes **5b** and **5d**, the trinuclear species **6a**,**b** show distinct resonances for the N bound methyl groups in their ^{1}H NMR spectra,. This is the consequence of Pd coordination to the NMe$_2$ group, which does not allow rotation around the C_α–N bond.

Attempts to extend the reaction and coordinate the Pd framework with complexes **5a** and **5c** were unsuccessful. These latter differ from **5b** and **5d** in that they contain a xylyl group (Xyl = 2,6-Me$_2$C$_6$H$_3$) instead of a methyl as the N-substituent. The lack of coordination of **5a** and **5c** is presumably due to the the steric hindrance of the Xyl group.

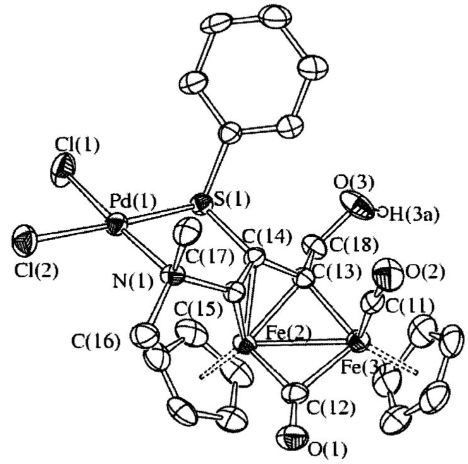


Figure 1. Molecular structure of **6b**, with key atoms labeled [all H-atoms, except H(3a), have been omitted for clarity]. Thermal ellipsoids are at the 30% probability level.

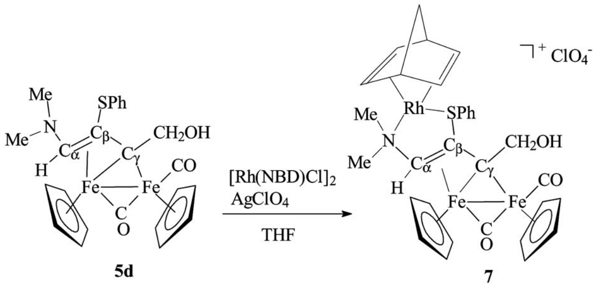
Table 1. Comparison of relevant bond lengths [Å] in **6b** and related enaminoalkylidene complexes.[a]

	6b	**I**	**II**
Fe(2)–Fe(3)	2.5482(17)	2.555(1)	2.5260(5)
Fe(3)–C(11)	1.755(10)	1.729(6)	1.733(3)
C(11)–O(2)	1.125(11)	1.157(7)	1.149(4)
Fe(2)–C(12)	1.921(9)	1.849(7)	1.851(3)
Fe(3)–C(12)	1.941(9)	2.012(6)	1.983(3)
C(12)–O(1)	1.152(10)	1.183(7)	1.192(3)
Fe(2)–C(13)	1.981(8)	1.979(6)	1.968(3)
Fe(3)–C(13)	1.950(8)	1.977(6)	1.979(2)
Fe(2)–C(14)	2.004(8)	2.070(6)	2.082(3)
Fe(2)–C(15)	2.062(7)	2.299(6)	2.201(3)
C(13)–C(14)	1.430(10)	1.441(8)	1.433(4)
C(14)–C(15)	1.430(10)	1.408(5)	1.413(4)
C(15)–N(1)	1.490(9)	1.375(8)	1.398(3)
C(14)–S(1)	1.795(8)	–	–
Pd(1)–N(1)	2.067(6)	–	–
Pd(1)–S(1)	2.255(2)	–	–
Pd(1)–Cl(1)	2.305(3)	–	–
Pd(1)–Cl(2)	2.306(2)	–	–

[a] **I** = [Fe_2{μ-η^1:η^3-C(Tol)CH=CHNMe$_2$}(μ-CO)(CO)(Cp)$_2$];[12a] **II** = [Fe_2{μ-η^1:η^3-C(Me)C(Me)=CHN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$].[18]

Further studies were aimed at the coordination of rhodium. Like palladium, rhodium is one of the most widely used transition metals in homogeneous catalysis and the number of complexes so far investigated is huge. Nevertheless, the synthesis of new ambidentate ancillary ligands is a persistent goal, and includes the design of new N,S ligands in order to provide the most appropriate steric and electronic coordination properties.[19]

The complex $[Rh(NBD)Cl]_2$ (NBD = norbornadiene), which is commonly used as precursor for square-planar Rh^I complexes, was treated with $AgClO_4$, in thf solution, to remove the chloride ions and generate a coordinatively unsaturated species that might be reactive towards **5d**. This procedure yielded the trinuclear complex $[Rh(NBD)(\kappa^2\text{-}N,S\text{-}\mathbf{5d})][ClO_4]$ (**7**; Scheme 4).

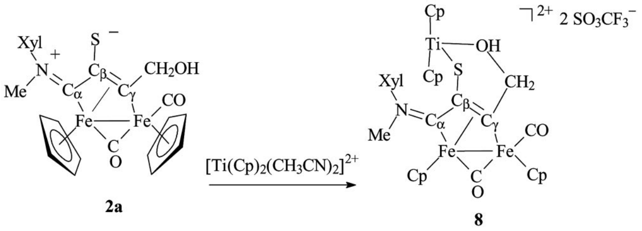


Scheme 4.

Compound **7** is stable in the solid state but decomposes slowly in solution (in CH_3COCH_3, CH_3CN, or CH_3NO_2). This behavior contributed to the failure of our efforts to obtain suitable crystals for X-ray diffraction. Complex **7** was therefore characterized by analytical and spectroscopic techniques only. The NMR spectra show one set of signals, thus indicating the presence of one single isomer. The coordination of the Rh(NBD) framework was confirmed by the shift of the ^1H and ^{13}C NMR resonances of the norbornadiene ligand, as unambiguously identified by two-dimensional COSY, HSQC, and HMBC experiments. As expected, all hydrogens of the NBD ligand are nonequivalent, with the exception of the CH_2 geminal hydrogens. The signals due to the remaining part of the complex (the "organometallic ligand" **5d**) closely resemble those observed in **6b**, where the same organometallic ligand is coordinated to Pd. Characteristic features are the inequivalence of the *N*-methyl groups and the high-field shifted resonance due to the C_α–H hydrogen, which suggests that the coordination mode of **5d** is identical in the Pd and Rh complexes. The IR absorptions for the terminal and bridging CO move to higher frequencies (ν_{CO} at 1971 and 1781 cm^{-1} vs. 1933 and 1770 cm^{-1} in **5d**) due to coordination to the cationic rhodium moiety.

Complexes **5c** and **5d**, which contain a CH_2OH group, have a further donor atom (O) in addition to S and N which is potentially able to coordinate a metal atom. The organometallic species **5c**,**d** should therefore also act as tridentate ligands, or as S,O chelates. The observed preference for N,S chelation with Rh^I and Pd^{II} is the rather obvious consequence of the "soft" character of the two metal ions and steric arguments which make three-coordination very unlikely. Attempts to test the coordination ability of the OH group would require a different and more oxophilic transition metal, such as titanium. The species we decided to study were $[TiCp_2Cl_2]$ and $[TiCp_2(CH_3CN)_2][SO_3CF_3]_2$. Our interest in the coordination of a titanocene framework also came from the fact that titanocene dichloride and its derivatives have emerged as important new antitumoral agents, and that much attention is currently being directed to investigating the replacement of chlorides with amino acid ligands (essentially N, O, and S ligands) in order to elucidate the mechanisms for delivery of Ti to cancer cells.[20]

Unfortunately, attempts to coordinate $TiCp_2$ to species **5c** and **5d** were unsuccessful as the organometallic ligands proved unreactive with respect to either $[TiCp_2Cl_2]$ or the solvate complex $[TiCp_2(CH_3CN)_2][SO_3CF_3]_2$. However, among the "organometallic ligands" mentioned in this paper, the zwitterionic compounds of type **2** (shown in Scheme 1) appeared to be better candidates, at least compared to **5c** and **5d**, for producing O,S coordination for the following reasons: a) the $C_\alpha N(Me)(R)$ group displays some aminocarbene character and, consequently, the N atom has reduced donor properties; b) the zwitterionic nature of the ligand assigns the negative charge to the S atom, which becomes a good donor. The overall result should favor chelating S,O vs. N,S coordination. In light of these considerations, we studied the reaction of **2a** with $[TiCp_2(CH_3CN)_2]$, generated from $[TiCp_2Cl_2]$ upon treatment with $Ag(SO_3CF_3)$ in CH_3CN solution. This reaction formed the trinuclear complex **8** (Scheme 5).

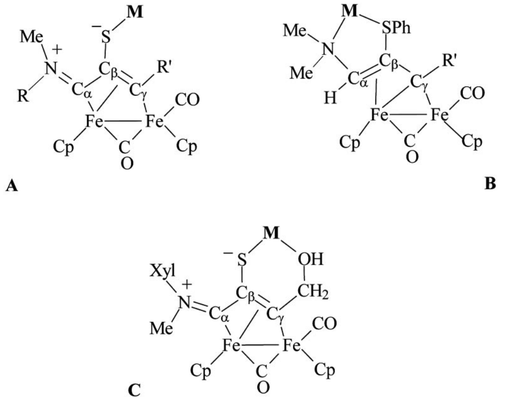


Scheme 5.

Complex **8** has been identified on the basis of elemental and spectroscopic analyses. Unfortunately, attempts to grow crystals suitable for X-ray diffraction were unsuccessful, therefore the molecular geometry shown in Scheme 5 is tentatively proposed on the basis of the spectroscopic data and on the following considerations. Chelation rather than mono-coordination of the $TiCp_2$ unit is likely to occur and involve the S atom. Indeed, dithiolate ligands[21] as well as mixed ambidentate ligands (P,S)[22] and (N,S)[23] are known to coordinate the Cp_2Ti unit. Analogies can also be envisaged with the anionic Fischer-type carbene complex $[(CO)_5Cr{=}C(R)O]^-$ (R = thiazolyl), which has been found to act as a bidentate N,O ligand with respect to $TiCp_2$.[24] In this case, the similarities include the fact that one coordination site is provided by an oxygen atom and that the ligand is an organometallic compound rather than a simple organic molecule. In complex **8**, the non-equivalence of the NMR signals attributable to the Cp ligands bound to Ti is consistent with bidentate coordination, which provides an unsymmetrical environment around the TiCp$_2$ unit. Coordination of TiCp$_2$ to the N atom can be excluded in light of the considerations discussed above regarding the lack of coordination properties of the iminium group in the zwitterionic complex **2a**. The iminium group undergoes little changes in the transformation from **2a** to **8**, as evidenced by the ^{13}C NMR resonance of the C$_α$ carbon, which is observed at δ = 225 ppm in **8**, close to the value of δ = 236 ppm for the precursor **2a**.

Conclusions

Diiron complexes bearing bridging functionalized C$_3$ organic frameworks containing N,S donor atoms that are potentially able to coordinate unsaturated metal fragments and act as "organometallic ligands" have been prepared. Their coordination ability can be appropriately tuned through appropriate transformations. Thus, vinyliminium zwitterionic complexes **2** almost exclusively act as monodentate S ligands, since the iminium N atom has no donor properties, and form type **A** complexes (Scheme 6). Conversely, the enamino-alkylidene complexes **5** behave as heterobidentate ligands and display chelating properties with respect to Pd and Rh (**B**, Scheme 6). Moreover, the bridging ligand can also contain OH as an oxygen donor functionality, in addition to S and N, which makes an S,O bidentate coordination possible (**C**, Scheme 6).



Scheme 6.

Our results show the great versatility of these diiron organometallic species due to the large number of transformations which can easily be performed at the bridging ligand. A further point to be noted is the effectiveness of the complexes as bidentate S,N organometallic ligands. These contain hard and soft donors along with a diiron backbone, with its own electronic and steric characteristics. Their combination might provide unusual activation effects on the Pd or Rh complexes, with potential applications in homogeneous catalysis. These possibilities are currently under investigations and will be the subject of future reports.

Experimental Section

General: All reactions were routinely carried out under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatographic separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. IR spectra were recorded at 298 K with a Perkin–Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed with a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K with a Mercury Plus 400 instrument. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The spectra were fully assigned by DEPT experiments and ^{1}H,^{13}C correlation from gs-HSQC and gs-HMBC experiments.[25] NOE measurements were recorded using the DPFGSE-NOE sequence.[26] All reagents were commercial products (Aldrich) of the highest purity available and were used as received. Compounds **2a**[8] and **3a–d**[9] were prepared by published methods.

Synthesis of [Fe$_2${μ-η^1-η^3-C$_γ$(R′)C$_β$(SPh)=Cα(H)N(Me)(R)}(μ-CO)(CO)(Cp)$_2$] (R = Xyl, R′ = Me, 5a; R = Me, R′ = Me, 5b; R = Xyl, R′ = CH$_2$OH, 5c; R = Me, R′ = CH$_2$OH, 5d): A thf solution (10 mL) of complex **3a** (120 mg, 0.162 mmol), was treated with NaBH$_4$ (60 mg, 1.58 mmol) and the resulting mixture was stirred for 30 min. Removal of the solvent and chromatography of the residue on an alumina column, with CH$_2$Cl$_2$ as eluent, gave a brown band corresponding to **5a**; yield 78 mg (81%). C$_{31}$H$_{31}$Fe$_2$NO$_2$S (593.34): calcd. C 62.75, H 5.27; found C 62.80, H 5.16. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = ν(CO) 1929 (vs), 1753 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.98–6.99 (m, 8 H, C$_6$H$_5$ and Me$_2$C$_6$*H*$_3$), 4.80, 4.32 (s, 10 H, Cp), 3.16 (s, 3 H, NMe), 2.68, 2.01 (s, 6 H, *Me*$_2$C$_6$H$_3$),0.98 (s, 1 H, C$_α$H) ppm. ^{13}C NMR (CDCl$_3$): δ = 269.5 (μ-CO), 218.8 (CO), 190.8 (C$_γ$), 155.0–125.9 (C$_{arom}$), 107.5 (C$_α$), 87.9, 83.1 (Cp), 68.9 (C$_β$), 40.1 (NMe), 19.1, 18.3 (*Me*$_2$C$_6$H$_3$) ppm.

Complexes **5b**–**d** were obtained by the same procedure described for **5a**, by treating **3b** (150 mg), **3c** (120 mg), and **3d** (150 mg), respectively, with NaBH$_4$.

5b: Yield 96 mg (83%). C$_{24}$H$_{25}$Fe$_2$NO$_2$S (503.03): calcd. C 57.25, H 5.01; found C 57.30, H 4.99. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = ν(CO) 1931 (vs), 1770 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.45–7.05 (m, 5 H, C$_6$H$_5$), 4.82 4.58 (s, 10 H, Cp), 3.92 (s, 3 H, C$_γ$*Me*), 2.46 (s, 6 H, NMe$_2$), –0.10 (s, 1 H, C$_α$*H*) ppm. ^{13}C NMR (CDCl$_3$): δ = 271.5 (μ-CO), 217.2 (CO), 185.3 (C$_γ$), 140.0 (*ipso*-C$_6$H$_5$), 129.0, 126.0, 125.2 (C$_6$H$_5$), 95.5 (C$_α$), 87.4, 82.8 (Cp), 83.6 (C$_β$), 46.6 (NMe$_2$), 41.9 (C$_γ$*Me*) ppm.

5c: Yield 75 mg (78%). C$_{31}$H$_{31}$Fe$_2$NO$_3$S (609.07): calcd. C 61.10, H 5.13; found C 61.04, H 5.17. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = ν(CO) 1934 (vs), 1755 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.01–7.04 (m, 8 H, C$_6$H$_5$ and Me$_2$C$_6$*H*$_3$), 6.61, 5.49 (m, 2 H, C*H*$_2$OH), 4.85, 4.40 (s, 10 H, Cp), 3.21 (s, 3 H, NMe), 2.73, 1.99 (s, 6 H, *Me*$_2$C$_6$H$_3$), 1.12 (s, 1 H, C$_α$H) ppm; *OH signal not observed.* ^{13}C NMR (CDCl$_3$): δ = 270.1 (μ-CO), 219.0 (CO), 191.5 (C$_γ$), 154.4–126.2 (C$_{arom}$), 109.3 (C$_α$), 88.6, 83.8 (Cp), 75.4 (CH$_2$OH), 69.2 (C$_β$), 41.2 (NMe), 20.0, 17.9 (*Me*$_2$C$_6$H$_3$) ppm.

5d: Yield 95 mg (82%). C$_{24}$H$_{25}$Fe$_2$NO$_3$S (519.03): calcd. C 55.52, H 4.85; found C 55.63, H 4.73. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = ν(CO) 1933 (vs), 1770 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.31–7.07 (m, 5 H, C$_6$H$_5$), 6.75, 5.56 (dd, $^2J_{H,H}$ = 11.1, $^3J_{OH}$ = 4.5 Hz, 2 H, C*H*$_2$OH), 4.84, 4.59 (s, 10 H, Cp), 2.46 (s, 6 H, NMe$_2$), 0.29 (s, 1 H, C$_α$H) ppm; *OH signal not observed.* ^{13}C NMR (CDCl$_3$): δ = 271.8 (μ-CO), 217.0 (CO), 189.4 (C$_γ$), 140.3 (C$_{ipso\ Ph}$), 129.0, 126.0, 125.1 (C$_{arom}$), 101.0 (C_α), 87.2, 83.0 (Cp), 85.7 (C_β), 76.6 (CH_2OH), 45.4 (NMe_2) ppm.

Synthesis of [PdCl$_2$(κ^2-*N*,*S*-5b)] (6a) and [PdCl$_2$(κ^2-*N*,*S*-5d)] (6b): A solution of **5b** (R = CH_3; 100 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of [PdCl$_2$(CH_3CN)$_2$] (52 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred at room temperature for 2 h. Removal of the solvent gave a solid residue, which was washed Et_2O (3 × 5 mL) and dried under reduced pressure to afford **6a** as a brown solid; yield 125 mg (91%). $C_{24}H_{25}Cl_2Fe_2NO_2PdS$ (678.87): calcd. C 42.42, H 3.71; found C 42.50, H 3.68. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(CO) 1964 (vs), 1796 (s) cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 7.96–7.20 (m, 5 H, C_6H_5), 5.29, 5.23 (s, 10 H, Cp), 4.04 (s, 3 H, C_γMe), 3.01, 2.51 (s, 6 H, NMe), –0.52 (s, 1 H, C_αH) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 264.2 (μ-CO), 214.1 (CO), 191.8 (C_γ), 130.9–127.7 (C_{arom}), 94.9 (C_α), 90.4, 87.3 (Cp), 85.2 (C_β), 56.3, 55.1 (NMe), 37.2 (C_γMe) ppm.

Compound **6b** was obtained following the same procedure described for **6a** by treating **5d** (100 mg, 0.19 mmol) with [PdCl$_2$(CH_3CN)$_2$]; yield 123 mg (93%). $C_{24}H_{25}Cl_2Fe_2NO_3PdS$ (694.87): calcd. C 41.45, H 3.63; found C 41.39, H 3.67. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(CO) 1966 (vs) cm^{-1} 1799 (s) cm^{-1}. ^{1}H NMR ([D$_6$]-acetone): δ = 7.99–7.21 (m, 5 H, C_6H_5), 6.25, 5.88 (m, 2 H, CH_2OH), 5.34, 5.19 (s, 10 H, Cp), 4.73 (br., s, 1 H, OH), 3.04, 2.49 (s, 6 H, NMe_2), –0.59 (s, 1 H, C_αH) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 264.0 (μ-CO), 214.3 (CO), 191.3 (C_γ), 131.2–127.5 (C_{arom}), 92.4 (C_α), 89.9, 86.1 (Cp), 85.5 (C_β), 74.5 (CH_2OH), 56.3, 55.8 (NMe_2) ppm.

Synthesis of [Rh(NBD)][(κ^2-*N*,*S*-5d)][ClO$_4$] (7): $AgClO_4$ (41 mg, 0.20 mmol) was added to a thf solution (10 mL) of [Rh(NBD)Cl]$_2$ (45 mg, 0.098 mmol) at room temperature. The mixture was stirred in the dark for 20 min, then filtered through a celite pad to remove the insoluble AgCl. The resulting yellow solution was then treated with a thf solution (10 mL) of **5d** (102 mg, 0.20 mmol) and stirred for 3 h at room temperature. Removal of the solvent gave an orange-brown solid, which was washed with Et_2O (2 × 5 mL) to give **7** (140 mg, 88%). $C_{31}H_{33}ClFe_2NO_7RhS$ (813.77): calcd. C 45.76, H 4.09; found C 45.80, H 4.04. IR (thf): $\tilde{\nu}$ = ν(CO) 1971 (vs), 1781 (s) cm^{-1}. ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.66–7.40 (m, 5 H, C_6H_5), 6.23, 5.88 (m, 2 H, CH_2OH), 5.36, 5.24 (s, 10 H, Cp), 5.02, 4.84, 4.82, 4.32, 4.13, 4.04 (br., s, 6 H, NBD), 4.50 (br. s, 1 H, OH), 2.71, 2.49 (s, 6 H, NMe_2), 1.45 (m, 2 H, NBD), –0.55 (s, 1 H, C_αH) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 265.9 (μ-CO), 216.9 (CO), 191.6 (C_γ), 131.4–128.8 (C_{arom}), 93.6 (C_α), 90.5 (Cp), 87.7 (C_β), 87.2 (Cp), 74.3 (CH_2OH), 73.4 72.4, 62.3 58.6, 51.9, 51.4 (CH, NBD), 64.0 (CH_2, NBD), 51.1 (NMe_2) ppm.

Synthesis of [Ti(Cp)$_2$(κ^2-O,S-2a)][SO$_3$CF$_3$]$_2$ (8): Ag(SO_3CF_3) (155 mg, 0.60 mmol) was added to a solution of [Ti(Cp)$_2$Cl$_2$] (75 mg, 0.30 mmol) in CH_3CN (15 mL). The reaction mixture was stirred for 30 min at room temperature in the dark, and then filtered through a celite pad. The solvent was evaporated under reduced pressure and the solid residue containing [Ti(Cp)$_2$(CH_3CN)$_2$][SO$_3$CF$_3$]$_2$ was redissolved in CH_2Cl_2 (10 mL). A solution of **2a** (160 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) was then added and the resulting mixture stirred for 3 h. Removal of the solvent gave a brown solid, which was washed with Et_2O (3 × 5 mL) to give **8**; yield 250 mg (83%). $C_{37}H_{35}F_6Fe_2NO_9S_3Ti$ (1007.0): calcd. C 44.11, H 3.50; found C 44.16, H 3.45. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(CO) 1998 (vs), 1820 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.55–7.20 (m, 3 H, $Me_2C_6H_3$), 7.01, 5.80 (d, $^2J_{H,H}$ = 13.8 Hz, 2 H, CH_2OH), 6.72 (br., OH, 1 H, s), 6.53, 6.43 (s, 10 H, TiCp), 5.77, 5.12 (s, 10 H, FeCp), 3.90 (s, 3 H, NMe), 2.77, 2.03 (s, 6 H, $Me_2C_6H_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 264.5 (μ-CO), 225.4 (C_α), 212.9 (CO), 193.3 (C_γ), 140.7 ($C_{ipso\ Xyl}$), 133.0, 132.2 (TiCp), 92.5, 91.3 (FeCp), 84.6 (C_β), 76.5 (CH_2OH), 49.5 (NMe), 17.9, 17.1 ($Me_2C_6H_3$) ppm.

X-ray Crystallography: Crystal data and collection details for **6b·CH$_3$CN** are reported in Table 2. The diffraction experiments were carried out with a Bruker APEX II diffractometer equipped with a CCD detector using Mo-K_α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[27] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[28] Hydrogen atoms were fixed at calculated positions and refined with a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. Similar *U* restraints were applied to the C-atoms [standard uncertainty (s.u.) 0.01]. The CH_3CN molecule is disordered over two positions. Disordered atomic positions were split and refined isotropically using one occupancy parameter per disordered group. Distances in the disordered CH_3CN molecule were restrained to 1.47 and 1.14 Å (s.u. 0.01) for C–C and C–N, respectively.

Table 2. Crystal data and experimental details for **6b·CH$_3$CN**.

Complex	**6b·CH$_3$CN**
Formula	$C_{26}H_{28}Cl_2Fe_2N_2O_3PdS$
Fw	737.56
T [K]	291(2)
λ [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	10.592(3)
b [Å]	11.572(3)
c [Å]	14.675(4)
α [°]	68.404(3)
β [°]	82.557(4)
γ [°]	64.784(3)
Volume [Å^3]	1512.3(6)
Z	2
D_c [g cm^{-3}]	1.620
μ [mm^{-1}]	1.809
F(000)	740
Crystal size [mm]	0.21 × 0.16 × 0.12
θ limits [°]	2.09–26.00
Reflections collected	15295
Independent reflections	5891 [R_{int} = 0.0679]
Data/restraints/parameters	5891/122/332
Goodness on fit on F^2	1.047
R_1 [$I > 2\sigma(I)$]	0.0705
wR_2 (all data)	0.2309
Largest diff. peak and hole [e Å^{-3}]	1.610/–1.109

CCDC-712586 contains the supplementary crystallographic data for **6b·CH$_3$CN**. 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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