Zwitterionic Organometallates

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Whereas ion-pairing has been long recognized as playing a key role in organometallic chemistry, the zwitterionic feature of organotransition metal complexes has only recently become an influential factor in the design of cationic metal catalysts. The prospective situation of reversed polarity, with metal fragments formally bearing an integral negative charge, may be envisaged. Besides the well-documented zwitterionic complexes derived from phosphonium ylides, other examples of zwitterionic organometallate complexes, formulated as such on the basis of structural, spectroscopic, or chemical evidence, have been reported in the recent literature and are reviewed here. They are classified according to the nuclearity of the anionic core and the nature of the cationic moiety, which can be a phosphonium, an ammonium, an iminium, a sulfonium, or a cationic organometallic fragment. The stabilization of the non-solvated charge separation is shown to arise from resonance and partial hapticity effects, hydrogen-type bonding, and tight intramolecular ion-pairing made possible by a back-folding of the ligand onto the metal center.

Introduction

Whereas dative bonds are generally assumed to govern the structures and reactivities of organometallic transition metal complexes as well as their catalytic properties, electrostatic interactions govern those of biochemical systems and enzymes. Of course, the borderline between the two realms is not quite so clear-cut. Indeed, metalloenzymes belong to the electrostatically-governed realm, whereas their models and biomimetic catalysts tend to rely on the auxiliary roles of dative interactions involving mainly electronegative atoms (O, N, S, etc.).[1] Conversely, electrostatic interactions play a definite albeit auxiliary role in organometallic complexes involving less electronegative atoms (C, P, H, etc.). Significantly, ion-pairing effects in organometallic species of both main group[2] and transition metals[3] have been widely studied. Nevertheless, intermolecular ion-pairing in solution remains a somewhat intangible phenomenon which is difficult to assess experimentally. In contrast, the intramolecular situation is chemically more relevant and is more easily appraised. Since the entropic effect is prone to favor rearrangements leading to the disappearance of the charge separation, the a priori fragile zwitterionic complexes merit special consideration. The purpose of this review is to classify a number of stable zwitterionic complexes selected from the recent literature, with particular emphasis on metallate species. In addition to the electrostatic energy of the intramolecular charge separation, the presence of a formal negative integral charge at an electropositive transition metal atom is apparently an intriguing feature of Lewis structures that are supposed to represent stable molecules (elusive zwitterionic excited states will not be discussed).[4] This misleading paradox can be rationalized by considering that the negative charge is actually more or less delocalized over the metal fragment and its auxiliary ligands (CO, X, Ph, etc.). Nevertheless, the *formal* presence of *integral* opposite charges linked through a path of covalent and dative bonds, located at the metal fragment and in a definite region of

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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the organic ligands, respectively, is explicitly emphasized as a peculiar feature by many authors: it is shown here to be a unifying feature of complexes designed for very different purposes.

Neglecting orbital components, the through-space electrostatic interaction corresponds to the energy of a formal point charge subjected to the isotropic electrostatic potential of the other. A number of cases may be distinguished depending on the relative positions of the formal charges. Firstly, if no non-zwitterionic connected Lewis structure can be drawn by resonance of the π-electrons, the complex will be classified as "mesoionic" or "truly zwitterionic". Secondly, if the opposite integral formal charges of the ion can be cancelled out by resonance in a non-zwitterionic mesomeric form, the complex will merely be partially zwitterionic. Three main situations are encountered:

(i) α-Dipole: This trivial situation corresponds to ionic ($M^{\pm}$,$X^{\mp}$) and semi-polar ($M^{\pm}$–$L^{\mp}$) bonds. It is trivially rendered degenerate by non-zwitterionic resonance forms (M–X, M=L, M↔L); the charge separation is thus weak and very formal.

(ii) β-Dipole: This situation can be mesoionic (M^{-}–X–Y^{+}) or otherwise ($M^{\pm}$=X–$Y^{\mp}$ ↔ M–X=Y) and corresponds to that of the well-studied derivatives of phosphonium ylide complexes M^{-}–CH_2–$^{+}PR_3$.[5]

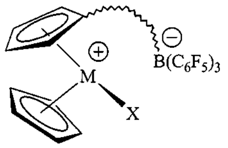
(iii) ω-Dipole: Here, the greater topological charge separation should a priori enhance the destabilization. Many push-pull transition metal complexes where the metal center plays the role of a donor or an acceptor have been prepared, particularly with a view to studying electron-transfer phenomena and to test their second-order nonlinear optical responses.[6] The ground states of such complexes can, however, essentially be described by the non-zwitterionic resonance form. In contrast, only zwitterionic complexes formulated by a main zwitterionic resonance form and stabilized by a secondary contribution from a non-zwitterionic resonance form will be dealt with here. Emphasis will be placed on stabilization stemming from inductive delocalization through σ-bonds, as well as from geometrical shortening of charge separation (back-folding of the ligand charge onto the metal charge).

After a brief overview of zwitterionic organometallic complexes of cationic metals that are currently the subject of growing interest for catalysis purposes, the review will then provide a survey of zwitterionic organometallic complexes exhibiting reversed polarity, i.e. with anionic transition metals, classified according to the nuclearity of the anionic fragment and the nature of the cationic terminus.

I. Zwitterionic Organometallic Complexes with Cationic Metals: A Brief Overview

Numerous neutral complexes containing a cationic transition metal center covalently bound to anions usually classified as weakly- or non-coordinating have been prepared, especially for catalysis purposes.

Catalysis in aqueous media is an active field of research of both industrial and academic relevance.[7] Water-soluble catalysts are obtained by tethering ionic functions to phosphane ligands of catalysts previously known to be effective in organic media. In this regard, the coordination sphere of the metal must be preserved, and the anion must be repelled at the periphery of the complex where it mainly interacts with the aqueous solvent. Although cationic functions such as ammonium can be used,[8] most water-solubilizing ligands bear anionic functions (carboxylate, sulfonate, etc.). Although the latter are often locally neutralized by a sodium cation, some cationic metal complexes such as the hydroformylation catalyst $Na_5[Co(CO)_3(P\{(CH_2)_nC_6H_4\text{-}p\text{-}SO_3\}_3)_2]$ can be formulated as zwitterionic.[9] Generally, however, the metal in the active species can be viewed as being formally neutral, ionicity being more important than zwitterionicity.



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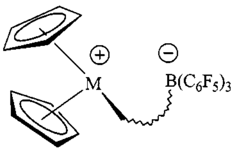

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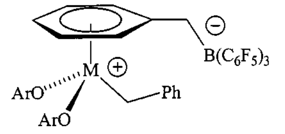

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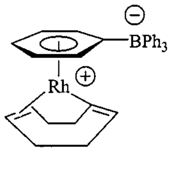
Besides water-solubilization effects, anionic end-groups can have more significant effects on catalytic activities. This is nicely illustrated by the design of efficient Group 4 metal catalysts for olefin polymerization. Since the pioneering work of Hlatky and Turner,[10] many research groups have focussed on the design of zwitterionic titanium, zirconium, and hafnium complexes bearing a borate functionality and acting as single-component polymerization catalysts. The state-of-the-art in cyclopentadienyl-containing zwitterionic catalysts (e.g. of types **1** or **2**) has periodically been reviewed.[11]

The active 14-electron cationic species must preserve its Lewis acidity as a target for the olefin, but as in the intermolecular situation, a sufficient degree of stabilization is required. Provided that it is allowed by the geometry, this is achieved by tight intramolecular $Zr^{+}\cdots H_2CB^{-}(C_6F_5)_3$ ion-pairing,[12] eventually assisted by α agostic interactions.[13] When the geometry enforces a large intramolecular charge separation, weak ArH→Zr^{+} or $^{-}$BArF:→Zr^{+} interactions serve to stabilize the structure. Zwitterionic complexes with a phenyl (instead of cyclopentadienyl) ancillary ligation (**3**) have also been reported, but proved to be poor polymerization catalysts owing to the π-donor properties of the aryloxy ligands.[14]

More generally, phenyl rings tethered to anionic borate centers can act as η^6-ligands towards other metals. Of particular relevance is Alper's zwitterionic rhodium(I) tetraphenylborate complex (**4**), which exhibits well-defined catalytic activity in various reactions (hydroformylation, hydrogenation, polymerization, etc.)[15] and, in particular, in the carbonylation of benzylic and allylic bromides under phase-transfer conditions.[16] Bis(catecholato)borate also acts as a η^6-coordinating anion in 18-electron cationic rhodium catalysts **5** for the hydroboration and diboration of alkenes.[17] Related hydridoruthenium complexes, such as **6**, have also been described, in which the boron atom of the η^6-tetraphenylborate ligand is even tilted away from the cationic ruthenium hydride.[18]



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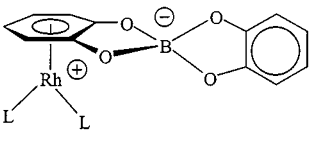

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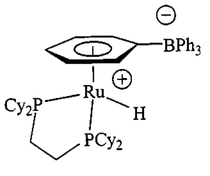

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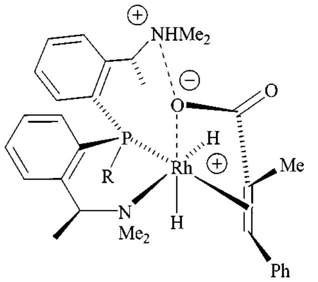
The subtle effects of ion-pairing phenomena in catalysis have been the topic of several studies, e.g. in the case of palladium-catalyzed allylic alkylation,[19] and zwitterionic intermediates have been shown to play a key role in stereoselective catalysis. Thus, in order to achieve enantioselective hydrogenation of substituted acrylic acid derivatives, Yamagishi and co-workers designed rather oxophilic rhodium complexes of chiral ω-aminophosphane ligands: the non-chelating amino group acted as a basic center that could deprotonate the carboxylic group of the substrate.[20] A separation of three formal charges was assumed to occur in the cationic intermediate **7**, and the intramolecular electrostatic interaction was claimed to enhance the facial selectivity of the alkene coordination.



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Similarly, Brunner et al. designed chiral rhodium complexes bearing chiral ligands where a ligand–substrate charge-transfer was found to control the stereoselectivity in asymmetric catalysis.[21]

Besides these applications in catalysis, the syntheses, structures, and properties of many zwitterionic organometallic complexes with cationic metal fragments have been studied. Consequently, the more rare situation of reversed polarity will now be considered in more depth.

II. Zwitterionic Organometallic Complexes with an Anionic Metal

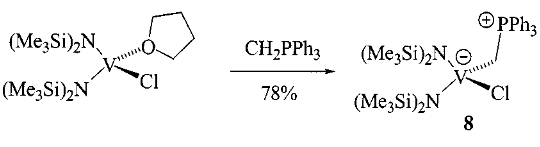
Among zwitterionic metallate complexes, a distinction can be made between mononuclear and dinuclear species.

II.1. Mononuclear Anionic Fragments

II.1.a. Phosphonium Complexes

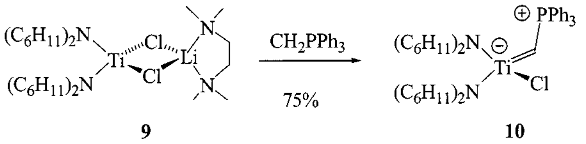
Most zwitterionic representations of organometallic complexes with an anionic metal center encountered in the literature correspond to the coordination of a phosphonium ylide or a conjugated equivalent. In these complexes, the charge separation is weak and corresponds to a β-dipole (M^-–CH_2–$^+PR_3$). It is remarkable that the metal–phosphorus distance is non-bonding: despite the possibility of adopting a formally non-zwitterionic Lewis topology [phosphorane alkylidene complex $M(\eta^2\text{-}CH_2{=}PR_3)$], this limiting dative bonding resonance form (which might be called a "haptomer form" by reference to a limiting π bonding resonance form called a "mesomer form") makes a negligible or very low contribution to actual equilibrium ground-state structures. The M^-–(η^1-CH_2–P^+) sequence can be regarded as a homologue of the simple M^-–$^+PR_3$ semi-polar or $M{\leftarrow}PR_3$ dative bond. Along the same lines, phosphoniocarbene metallate ($M^-{=}CH$–$^+PR_3$), phosphoniovinyl metallate (M^-–$CH{=}CH$–$^+PR_3$), and phosphonioacetylide metallate (M^-–$C{\equiv}C$–$^+PR_3$)[22a] structures are found to predominate over the non-zwitterionic mesomer forms in the descriptions of equilibrium ground-state complexes. Greater charge separations are also encountered in higher homologues of simple phosphane complexes $M{\leftarrow}PR_3$. The chemistry of these complexes has been thoroughly reviewed on several occasions,[5] hence only a few recent illustrative examples will be outlined here.

Phosphonium Ylide Complexes: The simplest method of preparation involves the substitution of a labile 2-electron ligand by the anionic end of an ylide. This is illustrated by the synthesis of the paramagnetic vanadium(III) zwitterionic complex **8** by substitution of a THF ligand by CH_2PPh_3 (Scheme 1).[22b] Despite the electrostatic attraction and the possibility of η^2-bonding, the V–C–P angle (128.6°) and the $V^-{\cdots}P^+$ distance (≈ 3.55 Å) are large. The analogous titanium(III) complex displays the same features.



Scheme 1

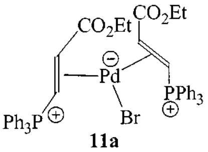
Phosphoniocarbene Metallate Complexes: The diamagnetic titanium(IV) complex **10** was obtained by oxidative coupling of an ylide with a titanium(III) complex **9** (Scheme 2).[22b] Analysis of the bond lengths by X-ray crystallography suggests that the non-zwitterionic phosphoranevinylidenyl limiting form $[(R_2N)_2(Cl)Ti–CH{=}PPh_3]$ makes only a minor contribution. This can be related to the pre-existence of a formal negative charge on the titanium atom in **9**, which can also be formulated as $[(R_2N)_2TiCl_2]^-$ $[Li(NMe_2CH_2)_2]^+$.



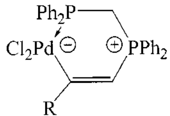
Scheme 2

Phosphoniovinyl Metallate Complexes: η²-Phosphonioalkene complexes such as **11a**,[23a] and η¹-β-phosphoniovinyl complexes such as **11b**,[23b] **12**,[24] or **13**,[25] among many others, are stabilized by a non-polar resonance form and often adopt a *trans* configuration across the C=C bond.

A *cis* configuration, as in **11b**, is enforced in metallacycles.[26] Stable 18-electron organometallic phosphonium zirconate complexes (**14**) have recently been described by Majoral and co-workers.[27] These were prepared by [3+2] cycloadditions of zirconaindene with alkynes (Scheme 3). The complexes were found to exhibit both an α- and a β-phosphonium configuration. Thus, several π-resonance paths can be envisaged, but the non-metallate resonance forms make only negligible contributions.



11a



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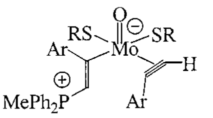

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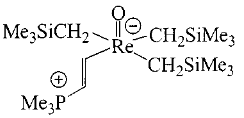

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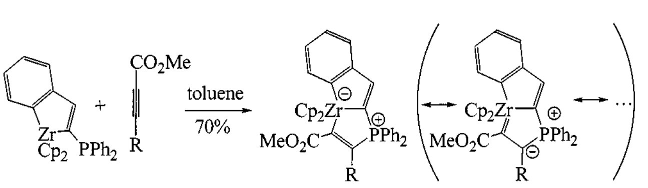
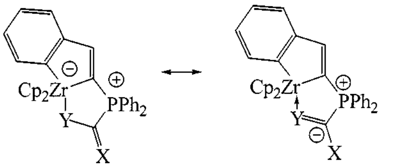
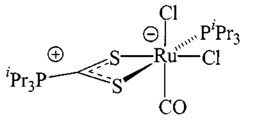


Scheme 3

This synthetic strategy has been extended to heteroallenes X=C=Y (X, Y = S, O, NR), leading to α-phosphoniovinyl complexes of type **15**.[28] Here, the Zr–Y bond lengths (Y = S, NR) were found to be longer than any known Zr–Y single bonds, thus indicating their dative character. A related type of covalent-dative zwitterionic ruthenate complex, **16**, has been obtained by insertion of CS_2 into a $iPr_3P{\rightarrow}Ru$ bond.[29]



15 X = O, S; Y = S, NR



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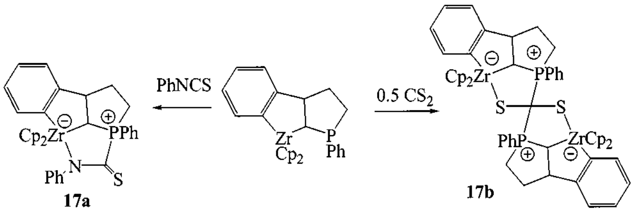
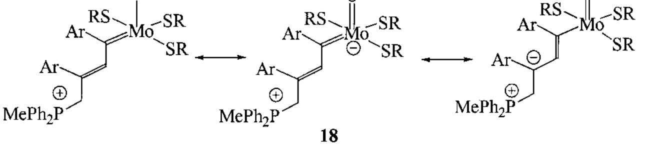
Finally, it must be pointed out that the phosphoniovinyl function is not necessary for stabilizing the zwitterionic structure. Reaction of X=C=S (X = S, NPh) with α-phospholane zirconaindane leads to either the tetracyclic phosphonium zirconate **17a** or to the spirocyclic bis-zwitterionic complex **17b** (Scheme 4).



Scheme 4

In all these cyclic phosphonium zirconate complexes, the $Zr^{-}\cdots P^{+}$ distances are in the typical range of 3.5–3.7 Å found in non-cyclic derivatives such as **8**.

Other Phosphonium Metallates: Zwitterionic mononuclear phosphonium metallate complexes with a large intrinsic charge separation can be stabilized by resonance. This is illustrated by comparing the phosphonium carbenemolybdate complex **18** (where the shortness of the Mo–C bond length is indicative of strong alkylidene character) with the related **12**, which has neither non-zwitterionic nor α-ylide resonance forms.[24]



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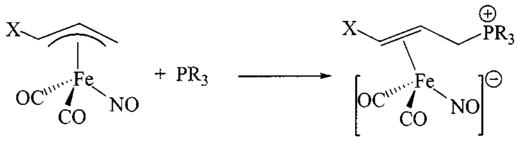
The γ-charge separation in allyl-type configurations is not greatly stabilized, as has previously been emphasized for the η^2-allylphosphonium ferrate complexes **19**,[30] but many related complexes have been isolated (Scheme 5).



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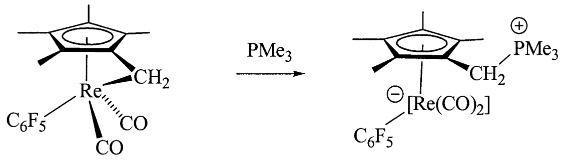
Scheme 5

The principle of the above reaction (cleavage of a metal–CH_2 bond by a phosphane) can be applied to the preparation of zwitterionic phosphonium rhenate complexes,[31] e.g. **20** (Scheme 6), where the link between the charges contains a cyclopentadienyl ligand as in [$^-$Cr(CO)$_3${η^5-$C_5H_4(CH_2P^+Et_3)$}][32] or in the bimetallic complex [Fe{η^5-$C_5H_4M^-(CO)_5$}(η^5-$C_5H_4P^+Ph_2Me$)].[33]



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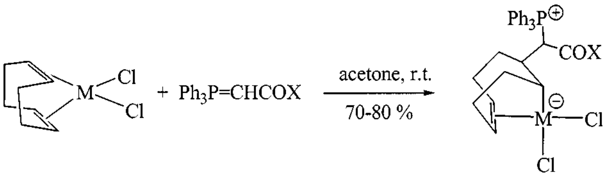
Scheme 6

In a similar process, cleavage of an Rh–C bond in a carborane-rhodium complex by nucleophiles leads to γ-zwitterionic phosphonium complexes.[34a] Owing to the fact that the $C_2B_9H_{11}^{2-}$ carborate is considered as an L_2X^- equivalent of the $C_5H_5^-$ ligand, the starting 18-electron Rh^{III} complex [{σ,η^5-10-[CH(*p*-tol)]-7,9-$C_2B_9H_{10}^-$}Rh$^+$(CO)(PPh$_3$)] is zwitterionic with a positive charge on the rhodium atom and a negative charge on the $C_2B_9H_{10}$ framework.[34b] Reductive cleavage by PEt$_3$ leads to the zwitterionic 18-electron Rh^I complex [{η^5-10-[Et$_3$P$^+$–CH(*p*-tol)]-7,9-$C_2B_9H_{10}^-$}Rh(CO)(PPh$_3$)], where no formal charge resides on the rhodium atom. The latter complex is therefore not a formal metallate.

Very recently, zwitterionic phosphonium organopalladate and organoplatinate complexes **21** with a δ non-conjugated charge separation were described. They were obtained through an unusual vinylogous nucleophilic attack of stabilized α-phosphonium ylides at a cyclooctadiene ligand in an *exo* fashion (Scheme 7).[35] Although the chloride ligands may be displaced by non-coordinating anions, the Pt–Cl 8distances in the crystal (2.3 or 2.4 Å depending on the *trans* effect of the facing ligand) are definitely bonding. IR and NMR data confirmed the formal zwitterionic nature of the complexes in solution.



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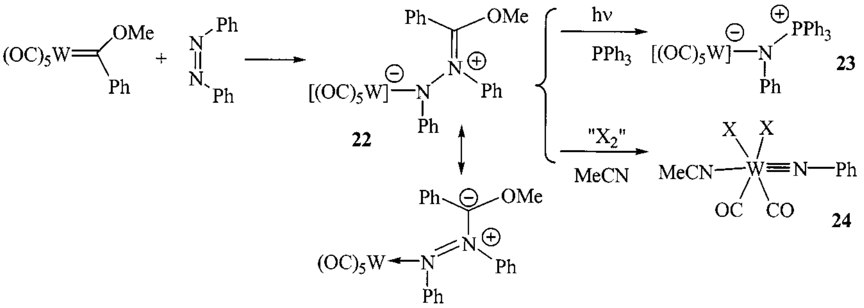
Scheme 7

II.1.b Mononuclear Ammonium and Iminium Metallate Complexes

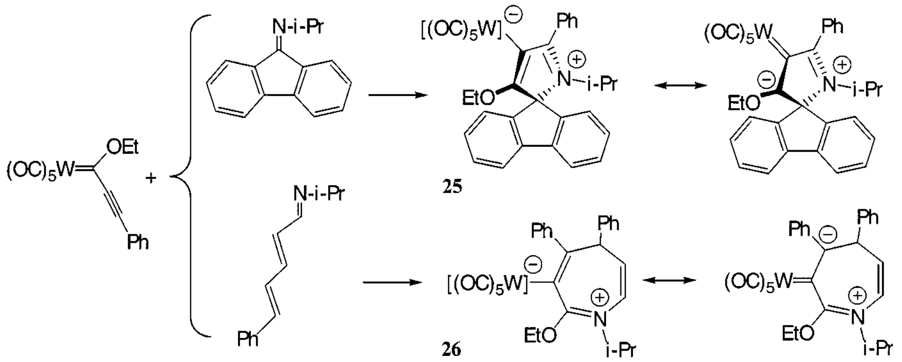
Interesting zwitterionic complexes, where the metal exhibits both a negative charge and a low formal oxidation state, are accessible from Fischer carbene complexes. This tendency is consistent with the analogy between the $(CO)_nM{=}C(R')$–OR fragment and the ester $O{=}C(R')O$–R fragment,[36] considering the resonance $O{=}C(R')O$–R ↔ O^-–$C(R'){=}^+OR$ to translate to $(CO)_nM{=}C(R')O$–R ↔ $(CO)_nM^-$–$C(R'){=}^+OR$. Such resonance arguments have been invoked to account for the α-CH acidities of Fischer-type carbene complexes $(CO)_5M{=}C(OR)(CH_2R')$.[37]

Unlike phosphonium ylides, "hydrazonium aza-ylides" are mesoionic. Their complexes have been prepared by formal metathesis of tungsten Fischer carbene complexes with *cis*-azobenzene.[38] The stereochemistry of complex **22** was deduced from its crystal structure, where the amido nitrogen atom was seen to be perfectly planar.[39] This planarity does not result from a p_π N:⇒W donation, but rather from steric constraints. The presence of the negative charge on the metal was supported by photochemical arguments, in particular by a shoulder in the UV/vis spectrum of the complex, which was interpreted as an MLCT transition. Under thermal or photochemical activation, complex **22** represents a source of the nitrene complex $(CO)_5W{=}NPh$, which can be trapped by PPh$_3$ to give the β-zwitterionic complex **23**, the zwitterionic (as opposed to apolar phosphinime) structure of which is suggested by its IR and ^{31}P-NMR data.[40] Under oxidative conditions, the zwitterionic amide complex **22** represents a precursor of imido tungsten complexes such as **24**, exhibiting various oxidation states.[41] The disappearance of the formal charge separation in the zwitterionic complex contributes to the driving force of the reaction (Scheme 8).



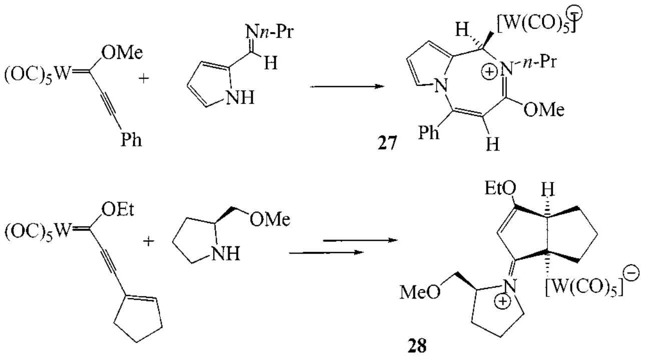
Scheme 8

The formation of the zwitterionic amido complex **22** involves nucleophilic attack of the nitrogen atom of azobenzene at the carbenic center, followed by a 1,3-shift of the $W(CO)_5$ fragment. Zwitterionic chromium complexes have also been generated from chromium carbene electrophiles,[42] and from other nitrogen nucleophiles such as ketenimines.[43] α,β-Unsaturated Fischer carbene complexes are susceptible to 1,2- or 1,4-attack by nitrogen nucleophiles, and subsequent rearrangements lead to zwitterionic iminium carbonylmetallate complexes **25–28**.[44] When the nucleophile contains an imino but not an amino group, the final complexes **25** or **26** may be mesoionic, although not necessarily at the metal center: the metal fragment is indeed bonded to an sp^2 carbon atom and the negative charge can be delocalized by π-resonance from the metal to the organic ligand (Scheme 9).[45]



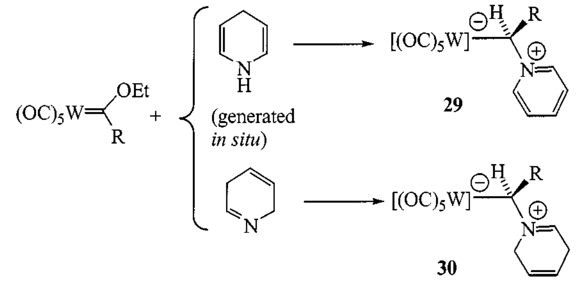
Scheme 9

In contrast, when the nucleophile contains a secondary amino group (Scheme 10), the metal in the iminium carbonylmetallate products **27** or **28** is bonded to an sp^3 carbon atom and the negative charge remains on the carbonylmetal fragment (as reflected in the corresponding $C–Cr^-$ or $C–W^-$ and $C{=}N^+$ bond lengths in the crystal structures).[46][47] The zwitterionic complexes are readily formed at room temperature and exhibit an astonishing degree of hydrolytic and thermal stability. The $W^- \cdots N^+$ separation can involve two bonds (iminium ylide complexes) or three bonds, but the positive charge of the exocyclic or endocyclic nitrogen atom is stabilized by resonance with α,β-conjugated C=C bonds and α- or γ-C–OR bonds. Nonetheless, the charge localization in complexes of type **28** also requires the support of electron-donating substituents at the nitrogen atom. Analogous dialkylphospheniums are unstable and rearrange to non-zwitterionic tungsten vinylphosphane complexes.



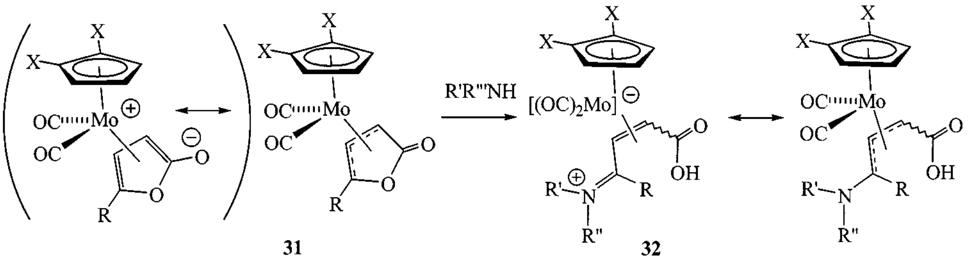
Scheme 10

Pyridinium ylide complexes of pentacarbonyltungsten, **29**, are true β-zwitterionic complexes where the metal fragment is bonded to an sp^3 carbon atom and retains its anionic charge in all possible π-resonance structures with the organic ligand. Such complexes are produced by the reaction of $(CO)_5M{=}C(OEt)R$ (M = Cr, W) with 1,4-dihydropyridine, formed in situ from 1-methoxycarbonyl-1,2-dihydropyridine and methyllithium (Scheme 11).[48] The stability of the zwitterionic complex might be ascribed to the aromaticity of the pyridinium product. However, non-aromatic 2,5-dihydropyridine analogues **30** have also been structurally characterized, demonstrating the presence of 2,5-dihydropyridine derivatives along with 1,4-dihydropyridine in the in situ formed reactant (Scheme 11).[49] The positive charge delocalization in **30** is restricted, and an X-ray analysis did not indicate any increased delocalization of the negative charge over the carbonyl ligand.

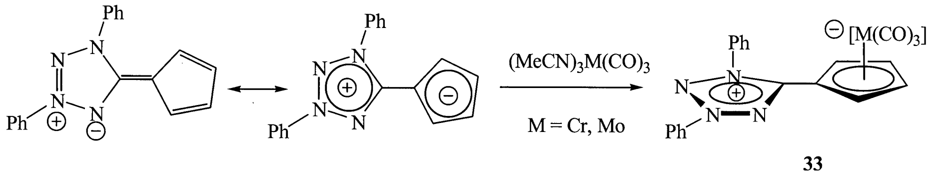


Scheme 11

In a reaction related to that leading to complex **19**, π-allyl ligands at $(CO)_2XMo^{II}$ centers undergo nucleophilic attack to afford zwitterionic intermediates.[50] In the case of η^3-lactonoyl ligands, despite the possible contribution of the reverse zwitterionic "haptomeric" structure in the electrophilic starting complex **31** (which has been explicitly invoked in related acyl π-allyl complexes),[51] the metal center is not directly attacked. The zwitterionic structure resulting from amine attack stabilizes by undergoing ring-opening (Scheme 12). According to IR spectroscopy and X-ray crystallography, the complexes **32** are better described by an iminium molybdate picture than by a non-zwitterionic structure.[52] The stability of **32** is somewhat surprising; the



Scheme 12

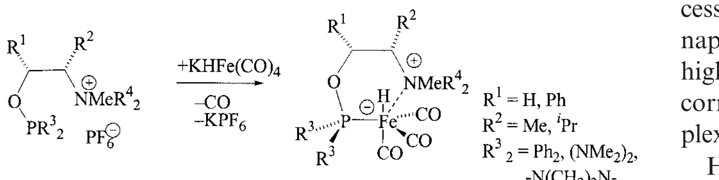


Scheme 13

anionic metal neither deprotonates the carboxylic acid function nor reacts with CH_3I.

Tetrazole is a cyclic imine that can act as an *N*-donor ligand in zwitterionic cationic metal tetrazolate complexes,[53] but it also provides the framework for a delocalized cationic moiety in zwitterionic complexes of reversed polarity (Scheme 13). The mesoionic character of olate, thiolate, selenolate, or cyclopentadienide 5-substituted tetrazolium can be transferred to zwitterionic Cr and Mo complexes **33**.[54] In the case of the cyclopentadienide derivative, the high-field shifts of the ^{1}H- and ^{13}C-NMR signals of the nuclei of the Cp ring and the decrease in the pivotal C–C stretching frequency in the IR spectrum upon complexation indicate that the resonance form with the shortest charge separation (N^+–N^-) tends to disappear in the complex. The latter is therefore truly zwitterionic. A similar conclusion can be drawn for olate, thiolate, and selenolate derivatives.

Zwitterionic metallate complexes with a positive charge completely localized at a quaternary ammonium center are not stabilized by resonance, but are less likely to lose the charge separation by a rearrangement of high-energy π-electrons. The intramolecular ion-pairing is thus expected to be very tight. Zwitterionic analogues of ammonium salts of phosphite and phosphinite hydridocarbonylferrates[55] have been studied in order to examine the possibility of a putative "chiral zwitterionic control strategy" in asymmetric reduction of prochiral ketones by chiral iron hydrides.[56] Chiral ammonium phosphinite ligands based on ephedrine or valinol skeletons ("ephosium", "valphosium", etc.) have thus been synthesized and reacted with $KHFe(CO)_4$ to give stable zwitterionic hydridotricarbonylferrate complexes **34** (Scheme 14).[57]



Scheme 14

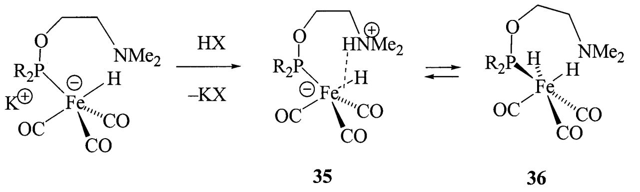
An unusual *cis*-H–Fe–P arrangement was suggested by IR and NMR data in solution, and was confirmed in the crystal. It was proposed that this rare feature was dictated by a stabilizing electrostatic back-folding of the [NMeR$^4_2$]$^+$ terminus onto the [FeH]$^-$ center. Indeed, a precise intramolecular $N^+Me_3\cdots{}^-HFe$ van der Waals contact between hydrogen atoms of the two moieties has been observed in the crystal. For steric reasons (hindrance of the equatorial carbonyl ligands), this dative-electrostatic chelation is not possible in a *trans*-H–Fe–P isomer. The intramolecular pairing was shown to be retained in solution, by a ^{1}H-^{1}H NOE between NMe_3^+ and HFe^-, and by the variation of the $|^2J(H,P)|$ coupling constant with the dielectric constant of the solvent, which also increases with temperature.[58] The latter correlation was proposed to reflect the effect of the dielectric constant on the average opening of hemilabile electrostatic edge $[HFe]^-\cdots{}^+[N]$ in the equilibrium:

open-[$^+$N~PFeH$^-$···solvent] $\rightleftarrows$ *closed*-[~N$^+$···$^-$HFeP~] + solvent

Ammonium cations were shown to form intermolecular contact ion-pairs with $[HFe(CO)_3L]^-$ anions, and a multisite docking of Me_4N^+ onto the external $[HFe(CO)_3P]^-$ anion was proposed to occur in THF in the vicinity of the [FeCO] and the [Fe–H] sites.[59] An intramolecular contact of this type has been found in the solid-state structure of **34**. It is also entropically favored in solution, even in polar solvents such as acetonitrile and dimethyl sulfoxide.

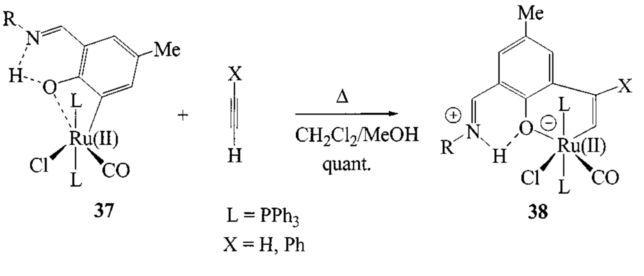
In conclusion, the true zwitterionicity and the flexibility of these complexes allow for stabilization through the adoption of otherwise rare structural and dynamic features. The chiral zwitterionic complexes are capable of reducing activated ketones, but do not give significant enantiomeric excesses. Chiral phosphonium phosphanes ("diopium", "binapium") have been devised as alternative ligands, but their higher basicities have so far prevented the isolation of the corresponding zwitterionic hydridocarbonylferrate complexes.[60][61]

Hydrogen or dihydrogen bonds $A^{\delta'-}\cdots{}^{\delta+}HX^{\delta-}$ involving transition metal centers (X = N, O, F; A = M, MY, MH), although electrostatic in nature, do not generally involve integral formal charges on both A and HX,[62] but some examples are worthy of mention. Transition metal complexes with a bond between a "proton" and a "hydride" $^{\delta-}$MH···HX $^{\delta+}$ are fascinating species corresponding to a heterolytic predissociation state of the dihydrogen molecule. In most cases, however, the charge on the metal is not formally –1 (the H ligands of neutral or even cationic transition metal hydrides are still refered to as "hydrides").[63] Protonation of an ω-aminophosphane hydridoferrate anion occurs at both nitrogen and iron sites (Scheme 15). In polar solvents at low temperatures, the zwitterionic structure **35** has been detected by ^{1}H-NMR, and measurements of the T_1 relaxation times for the NH$^+$ and FeH$^-$ ^{1}H nuclei at low temperatures allowed an estimation of the H···H distance of ca. 1.71 Å.[64] This value is typical for a dihydrogen bond, and was reproduced as the optimized distance in DFT calculations using the B3PW91 functional.[65] In less polar solvents and at higher temperatures, an equilibrium between the zwitterionic ammonium hydride structure **35** and the non-zwitterionic dihydride structure **36** was observed. DFT calculations showed the non-zwitterionic complex **36** to be more stable than **35** by 8 kcal mol^{-1} in vacuo, but that the order of stability is reversed on taking into account the dielectric constant of a polar solvent.



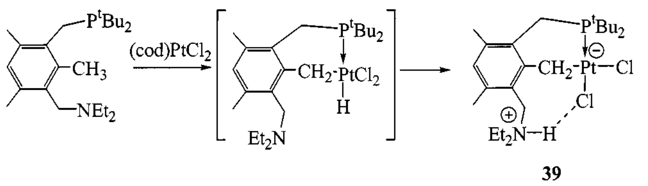
Scheme 15

More classically, hydrogen-type bonding can involve a halide or an oxygen atom instead of a hydride,[66] and occurs as a source of stabilization in truly zwitterionic complexes. The zwitterionic character of complex **38** arises from strain release following insertion into the four-membered metalla-oxetane ring of **37** (Scheme 16). Thus, the cyclic Ru–O bond in complex **37** is quite long (≈ 2.24 Å) and undergoes facile cleavage by ligands. The insertion of an alkyne into the adjacent Ru–C cyclic bond leads to a complex that features a much shorter Ru–O bond length (2.10 Å) with a definitely protonated nitrogen atom. This complex could be described by the zwitterionic structure **38**, featuring an NH···O hydrogen bond.[67]



Scheme 16

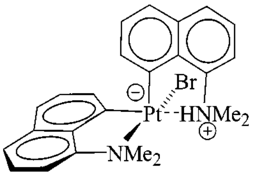
Milstein and co-workers reported that a non-zwitterionic Pt^{IV} complex produced by intramolecular C–H activation of a neutral Pt^{II} complex undergoes spontaneous stabilization through intramolecular proton-transfer to a pendant amino group to give the zwitterionic Pt^{II} complex **39** (Scheme 17).[68]



Scheme 17

The zwitterionic nature of **39** was established by X-ray crystallography. Thus, the chlorine atom involved in the hydrogen-bonding is tightly bound to the platinum atom (NH···ClPt ≈ 2.41 Å), the corresponding Pt–Cl bond being shorter (≈ 2.38 Å) than the others (≈ 2.41 Å).

This coordination mode represents the alkylplatinum analogue of the zwitterionic arylplatinum complexes described by van Koten and co-workers.[69] The authors showed that ammonium protons of zwitterionic platinate complexes can interact with either a Pt–Br bond or the formally anionic platinum atom. In the latter situation, the formal charge separation is shorter, but is still present in the platinate(II) structure **40**. The non-zwitterionic hydridoplatinum(IV) structure was ruled out on the basis of NMR data (downfield shift of the proton resonance, small coupling constants between the *ortho*-aromatic protons of the ligand and ^{195}Pt) and by its X-ray crystal structure (N–H ≈ 0.88 Å, Pt···HN ≈ 2.11 Å >> classical Pt–H bond lengths). The stability of the zwitterionic structure of **40** is not only due to the hydrogen bonding, but also to steric shielding of both the platinate center (from strong electrophiles such as MeI) and the ammonium center (from D$_2$O exchange).

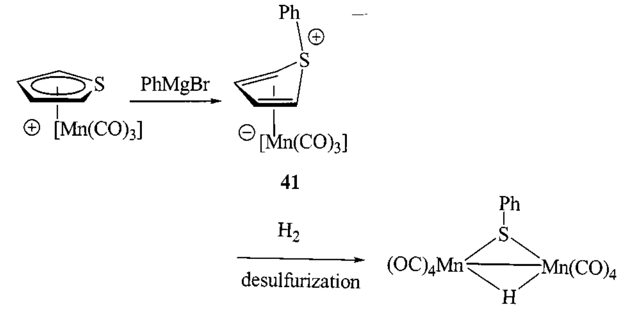


40

Borderline examples of zwitterionic ammonium metallate complexes are worthy of mention. Thus, zwitterionic 16-electron rhodium-carborate complexes have been prepared by substituting two 2-electron ligands of a neutral rhodium precursor {e.g. [RhBr(PPh$_3$)$_3$]} with a zwitterionic *nido*-carborate ligand (e.g. *nido*-7-*t*BuH$_2$N$^+$–7-CB$_{10}$H$_{10}^-$).[70] The product might a priori be formulated as an 18-electron rhodium(I) complex [(η^5-7-*t*BuH$_2$N$^+$–7-CB$_{10}$H$_{10}$)Rh$^-$Br(PPh$_3$)]. However, since the metallacarborane is not distorted from a triangular *closo*-icosahedral framework, the complex is actually a 16-electron cationic rhodium(III) complex [(η^5-7-*t*BuH$_2$N$^+$–7-CB$_{10}$H$_{10}^{2-}$)Rh$^+$Br(PPh$_3$)], in which both the Rh and N atoms are cationic and a double negative charge is delocalized over the carborane framework.

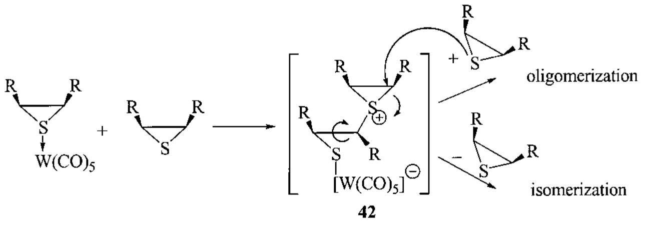
II.1.c. Sulfonium Metallate Complexes

Sulfonium metallate structures are of great relevance to the industrial challenge of petroleum desulfurization. Thus, thiophene derivatives can be hydrodesulfurized via zwitterionic sulfonium manganate(0) complexes **41** obtained by nucleophilic attack at the S atom of cationic η^5-thiophene species. A model of the above zwitterionic intermediate has been characterized by X-ray crystallography. Its structure reveals activation of both the manganese and sulfur atoms, which allows hydrogenolysis of the C–S^+ bonds (Scheme 18).[71]



Scheme 18

Zwitterionic sulfonium metallates occurring in catalytic processes cannot be isolated, but can be invoked as key intermediates. $W(CO)_5(NCMe)$ and $W(CO)_5$(thiirane) complexes have been found to catalyze desulfurization, ring-opening oligomerization, and isomerization of thiiranes $S(CHR)_2$ ($R = H$, Me),[72] and the intermediacy of zwitterionic species **42** resulting from an S_N2 reaction of a free thiirane sulfur atom at a coordinated thiirane carbon atom has been postulated (Scheme 19).



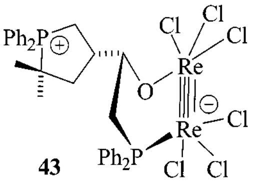
Scheme 19

II.1.d. Zwitterionic Oxonium Complexes

nido-Carborane complexes such as $[Mn(CO)_3\{\eta^5\text{-}7,8\text{-}C_2B_9H_{10}\text{–}10\text{-}O(CH_2)_4\}]$ have been described as zwitterionic. This representative complex has been characterized by X-ray crystallography, and has been shown to react with various nucleophiles to afford phosphonium and ammonium zwitterionic complexes with large charge separations. However, the dianion $C_2B_9H_{11}^{2-}$ is a complexing equivalent of the monoanion $C_5H_5^-$ and since the formally neutral manganese atom in $[Mn(CO)_3\{\eta^5\text{-}C_5H_5\}]$ obeys the 18-electron rule, the negative charge compensating the positive charge of the oxonium substituent is delocalized over the $C_2B_9H_{10}$ framework and not over the metal atom. Therefore, although the complex is indeed zwitterionic, it should not be regarded as a formal metallate species.[73]

II.2. Dinuclear Anionic Fragments

A negative charge can be delocalized over two or more metal fragments. Owing to the electropositivity of metals, this is a priori a destabilizing factor, but the metal–metal bond permits delocalization of the excess electron over twice as many auxiliary ligands (CO, Cl, etc.) on the anionic metals as in the corresponding mononuclear species. For example, in the nice zwitterionic complex of the chiral phosphonium ligand "isodiop", **43**,[74] the negative charge is delocalized through a quadruple rhenium–rhenium bond. Here, the X-ray crystal structure does not reveal any backfolding of the P^+ center onto the anionic metal.



43

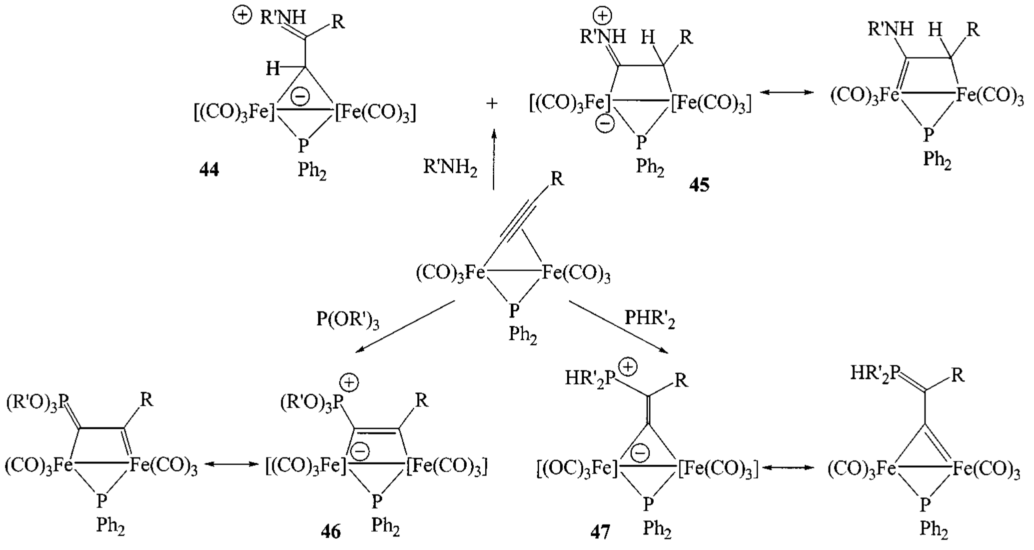
Homo- and heterobimetallic transition metal allenyl complexes with single metal–metal bonds provide frameworks for interesting zwitterionic organometallate complexes,[75] particularly in the case of diiron complexes. Nucleophilic additions at the μ-σ,π-acetylide ligand of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C_2R)$ afford various kinds of zwitterionic complexes, in which a negative charge is delocalized over the two iron centers (Scheme 20).

Short β charge separations, also shadded off by minor contributions from non-dipolar resonance forms,[76] occur in **45–47**, but γ charge separation occurs in the truly zwitterionic complex **44**.[77] The negative charge can also reside on (and polarize) substituted $Fe_2(CO)_5P$ cores as in the C_β-phosphonio-phosphane complex **48**[78] (Scheme 21) or in related C_α-phosphonio-phosphane complexes.[79]

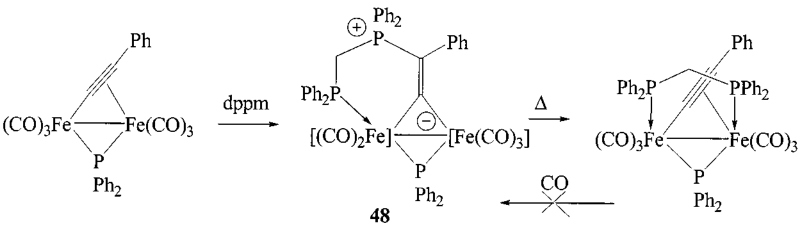
Related μ-σ,π-allenyl precursors generate similar phosphonium complexes,[80] but can also lead to a new type of mesoionic μ-η^2-propylene complex **49**,[81] which isomerizes to the non-dipolar complex **50** (Scheme 22).

Dinuclear phosphonium complexes with three-bond charge separation have long been characterized.[82] The X-ray crystal structure of complex **51** shows that the hydrocarbyl ligand adopts a μ-η^1:η^2 coordination mode (Scheme 23). The high-field shift of the ^{13}C-NMR signal of the C_α–Os center confirms the 18-electron rule and indicates that the osmium atom bears the negative charge which is no longer delocalized over the neutral 18-electron rhodium atom.[83]

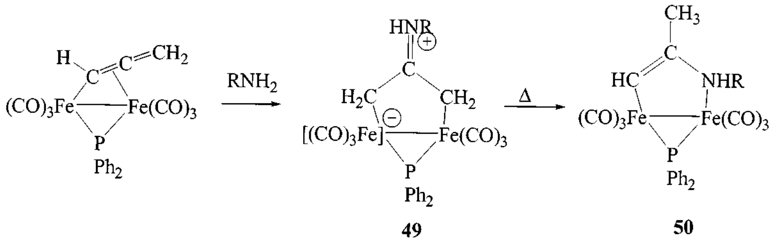
Among the Group 9 homodinuclear metallates, a complex of 2,3-bis(diphenylphosphanyl)maleic acid has been found to stabilize through formation of a zwitterionic cobaltate complex **52** at elevated temperatures (Scheme 24).[84] An 18-electron count for both the metal atoms indicates that the formal charges are separated by three bonds. This



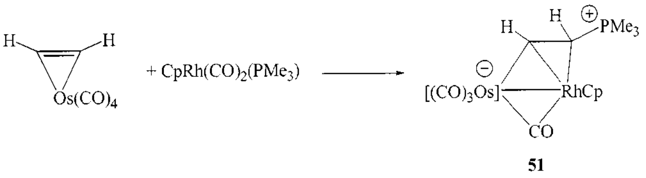
Scheme 20



Scheme 21

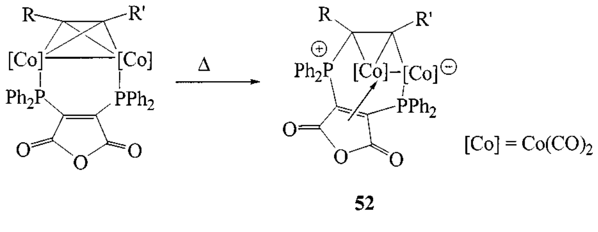


Scheme 22



Scheme 23

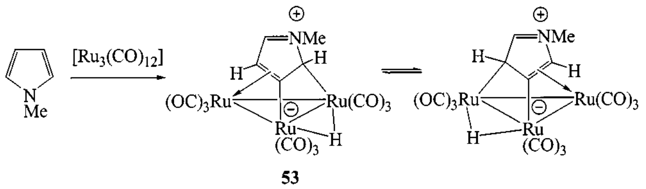
example does not represent a C-η^1-ylide complex, but rather a C,C-η^2-β-phosphoniovinyl complex, the non-coordinated analogue of which corresponds to complexes of types **12** and **13**.



Scheme 24

II.3. Trinuclear Anionic Fragments

Zwitterionic metallates of higher homonuclearity ($[Fe]_3^-$, $[Ti]_3^-$, $[Ru]_3^-$, etc.) have also been described, where the cationic charge is borne by either an appended metal fragment,[85] an iminium,[86] a phosphonium, or an ammonium group.[87] For example, the charge separation on the ruthenium cluster **53** has been evidenced by spectroscopy (ν_{CO} IR frequencies are lower than those found for classical non-zwitterionic related clusters) and by a strong solvent effect on the thermal stability the cluster. The charge delocalization over the three metal atoms also takes place dynamically in solution through rapid interconversion of isomers by

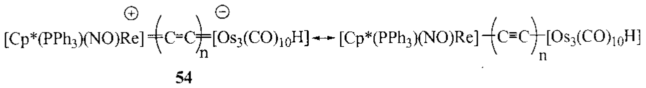


Scheme 25

concerted hydride shifts and small geometric displacements (Scheme 25).

III. Zwitterionic Complexes with both Anionic and Cationic Metals

Transition metals linked by a "wire" of sp carbon atoms are attracting a great deal of interest in the context of studies of electron-transfer between metals under various physicochemical stimuli. When the two metallic groups are different in electronegativity, a zwitterionic form can make a significant contribution to the ground state of the complex. For instance, in the rhenium–osmium bimetallic complex **54**, the zwitterionic cumulenic form is seen to make a significant contribution as opposed to the polyacetylenic form.[88]



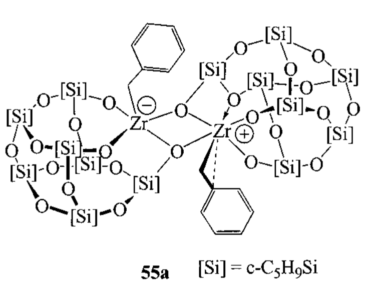
$[Cp^*(PPh_3)(NO)Re]^{\oplus}{=}\left(C{=}C\right)_n{=}[Os_3(CO)_{10}H]^{\ominus} \longleftrightarrow [Cp^*(PPh_3)(NO)Re]-\left(C{\equiv}C\right)_n-[Os_3(CO)_{10}H]$

54

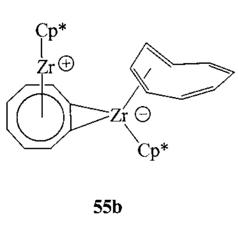
It is not the aim of this review to cover this large field; this section merely gathers together several examples of types of zwitterionic dinuclear complexes that can simply be described in terms of a static two-electron transfer from one metal to another on the basis of structural and spectroscopic data.

III.1. Zwitterionic Group 4 Metallates with an Appended Cationic Metal

It has previously been mentioned that both zwitterionic cationic zirconium and anionic zirconate complexes are known. The two charge states have been postulated as being present in the zirconium complexes **55a** and **55b**. Indeed, the dimeric silsesquioxane **55a** exhibits an asymmetric structure in the solid state.[89] A negative charge has been assigned to the zirconium atom bearing five oxygen ligands and one η^2-benzyl ligand. However, the comparable Zr–O bond lengths suggest that a non-zwitterionic limiting structure also contributes to the description of the complex. For the organo-bridged complex **55b**, the zwitterionic formulation was suggested by a reasonable electron count, showing two 16-electron Zr^{IV} and Zr^{II} atoms, and was confirmed by the diamagnetism of the complex.[90]



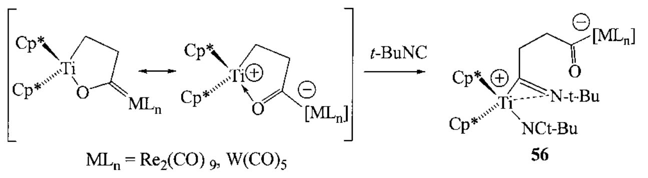
55a [Si] = c-C_5H_9Si



55b

III.2. Zwitterionic Group 5 Metallates with an Appended Cationic Metal

Alkyltitanium-rhenium and -tungstene complexes undergo insertion of *tert*-butylisocyanide to afford truly zwitterionic complexes of type **56**, in which the 18-electron metals are separated by a butanedioic bridge (Scheme 26). The reaction is favored by the existence of a zwitterionic resonance form of the starting complex.[91]



$ML_n = Re_2(CO)_9, W(CO)_5$

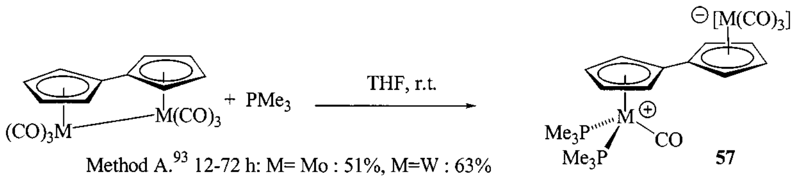
Scheme 26

1II.3. Zwitterionic Group 6 Metallates with an Appended Cationic Metal

Besides metal-substituted (π-arene)chromium complexes polarized by subtle resonance and inductive effects (e.g. $[\{\eta^1{:}\eta^6\text{-}C_6H_5(TiCp_2Cl)\}Cr(CO)_3]$),[92] zwitterionic bimetallic complexes of Group 6 metals are found in the fulvalene series. Homodinuclear complexes, in which the metals exhibit different CO vs. phosphane substitution patterns, can be prepared by several methods (A,[93] B,[94] or C[95]) from $(fulvalene)Mo_2(CO)_6$ and basic phosphanes. After metal–metal bond cleavage, the steric repulsion between the metal centers overrides the electrostatic attraction and results in a 180° rotation of the cyclopentadienyl metal moieties, which, in turn, leads to a *trans* arrangement of the opposite charges with respect to the cyclopentadienyl plane. The zwitterionic nature of these complexes, e.g. **57**, is evident from comparisons of their IR and NMR spectroscopic data, X-ray crystal structures, and chemical reactivity with those of related separated anionic and cationic complexes (Scheme 27).

Most notably, the molybdenum zwitterionic complex undergoes ring-slippage to give the neutral mononuclear η^4-fulvalene complex **58**, probably via an intermediate in which one of the molybdenum atoms has a 16-electron configuration (Scheme 28). This intermediate structure might also be regarded as a non-zwitterionic "haptomer" form of the complex, accounting for its stability and the electron communication between the two metals.

The use of electron-reservoir complexes such as [FeCp(arene)] can also serve to prepare heterodinuclear $^{-}[Mo,W]$–$[Fe,Ru]^{+}$-type zwitterions (**59**). Here, phosphane ligands selectively bind to the cationic Group 8 metal. The enhanced rate and selectivity of this reaction (Scheme 29) as compared with those of their homodinuclear counterparts can be rationalized in terms of the dissymmetry of the heterodinuclear system and has been verified by cyclic voltammetry experiments.

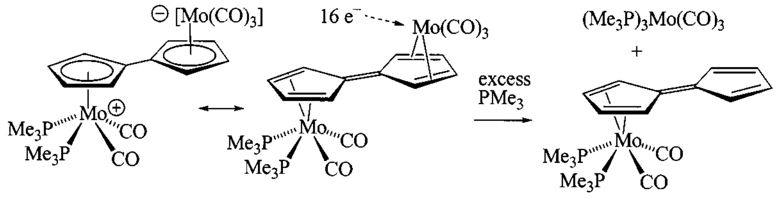


Method A.[93] 12-72 h: M= Mo : 51%, M=W : 63%

Method B.[94] cat. $[FeCp(C_6Me_6)]$, few minutes: M= Mo: 70%, M=W : 56%

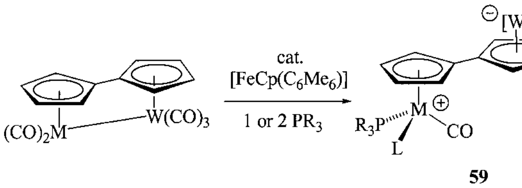
Method C.[95] Me_3NO, 10 min: M= Mo : 95%, M=W : 90%

Scheme 27



58

Scheme 28



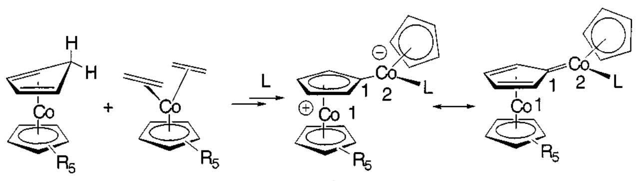
M = Fe, Ru
R = Me, OMe
L = CO, PR_3

59

Scheme 29

III.4. Zwitterionic Group 9 Metallates with an Appended Cationic Metal

Twofold C–H activation of the η^4-cyclopentadiene ligand in complexes by the homologous bis(ethylene) complex (Jonas' reagent) leads to dinuclear Co^I–Co^{III} complexes (**60**) (Scheme 30). X-ray crystal data ruled out the possibility of a metal–metal bond and the formal assignment of the oxidation states can be interchanged between the two metals by simple "haptomeric resonance". The relative contributions of these limiting structures have been carefully analyzed in terms of the π-acceptor vs. σ-donor character of the ligand L.[96] The C(1)–Co(2) distance is extremely short (average 1.87 Å) while the C(1)–Co(1) distance (average 2.20 Å) is longer than all the other (Cp)C–Co(1) distances (average 2.04 Å). Thus, although the occurrence of a cobaltocenium fragment is expected to be favored, the zwitterionic character is not pure. It nevertheless becomes quite important when L is an acceptor ligand.

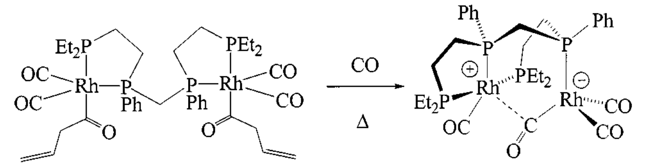


60

R_5= H_5, Me_5, $(Me_4)(Et)$ L = C_2H_4, CO, ^tBuNC, PMe_xPh_{3-x}, $P(OMe)_3$

Scheme 30

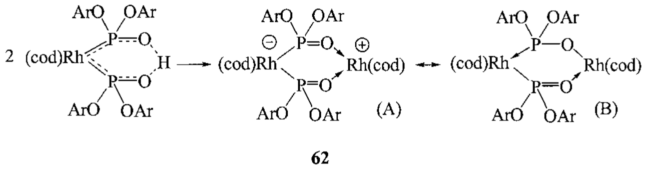
Potentially symmetrically bridged dinuclear complexes can exist as rearranged zwitterionic complexes. Thus, thermal activation of a symmetrical tetraphosphane diacyl dirhodium complex under CO pressure unexpectedly led to the disymmetrical dirhodium complex **61** (Scheme 31).[97] The zwitterionic character of **61** was ascertained by X-ray crystallography, which revealed a tetrahedrally coordinated anionic tricarbonylrhodium center facing a geometrically distorted cationic triphosphane rhodium center without an Rh–Rh bond. A semi-bridging carbonyl ligand accounts for the stability of the zwitterionic structure. This feature also results in an 18-electron count for both rhodium atoms in the $^-Rh{\approx}Rh^+$ structure without an Rh–Rh bond. The structure is also supported in solution by ν_{CO} IR and ^{31}P-NMR data.



61

Scheme 31

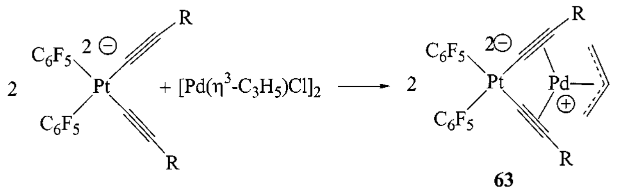
Dinuclear rhodium complexes can be formulated as zwitterionic on the basis of reactivity arguments. The acidic proton of a phosphito-phosphonato rhodium complex $[Rh^I]^-[H]^+$ can be removed by NaOH, but also by the basic Rh^I center of another identical molecule to give an intermediate $[Rh^I]^-[Rh^{III}H]^+$ salt, which reacts further to give the molecular salt $\{[Rh^I]^-[Rh^I]^+\}$, **62** (Scheme 32). The latter complex can therefore be regarded as a disymmetrical zwitterionic species, in which two "hard" oxygen atoms of the two equivalent phosphonate ligands point towards the hard cationic Rh atom, while the two "softer" phosphorus atoms point towards the softer anionic Rh atom. However, the driving force of the reaction relates to the participation of two equivalent non-zwitterionic forms (B).



Scheme 32

III.5. Zwitterionic Group 10 Metallates with an Appended Cationic Metal

Cationic π-allyl complexes of palladium and platinum react with dianionic platinate to give stable anionic bimetallic complexes **63** with a 2–/+ charge separation (Scheme 33).[98] X-ray, IR, and NMR analyses indicate that the metals communicate through π-bonds.



Scheme 33

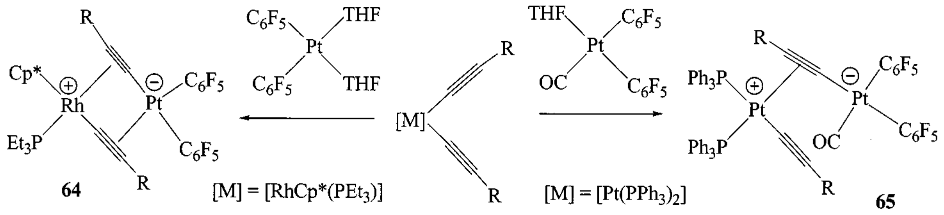
However, when the reactant is the twofold cationic [Cp* $Ir(PEt_3)(acetone)_2]^{2+}$ complex, the expected 2–/2+ charge separation is unstable and a non-zwitterionic product results from a migration of the σ-alkynyl ligands to the iridium atom.[99] In contrast, migration of alkynyl ligands from neutral bis(alkynyl)platinum complexes to neutral platinum or rhodium reactants can occur in the presence of suitable ligands, thereby leading to charge separation in complexes **64**[100] and **65** (Scheme 34).[101]

A similar process of migration of a chlorine ligand between two neutral complexes leads to the trimetallic zwitterionic complex **66**, in which the positive charge is delocalized over a dimetallic core (Scheme 35).[102]

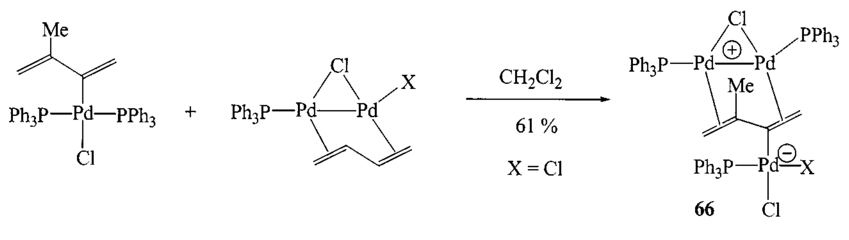
A zwitterionic monoanionic platinate complex with a cationic charge delocalized over a trinuclear platinum core has also been reported.[103] Trinuclear zwitterionic metallate complexes with a –2/+1/+1 charge separation on the metals may be prepared from a *trans*-dialkynylplatinate. The latter reacts with two equivalents of the cationic platinum reagent $[\textit{trans}\text{-}PtH(PEt_3)_2]^+$ to give the neutral zwitterionic trinuclear complex **67**, in which the doubly negative platinate center acts as a bridging unit (Scheme 36). Although low stability in solution prevented characterization by ^{13}C-NMR, the zwitterionic nature could be ascertained from IR and X-ray diffraction data, although a contribution of a "haptomer" vinylidene structure has been suggested.[104]

Conclusion

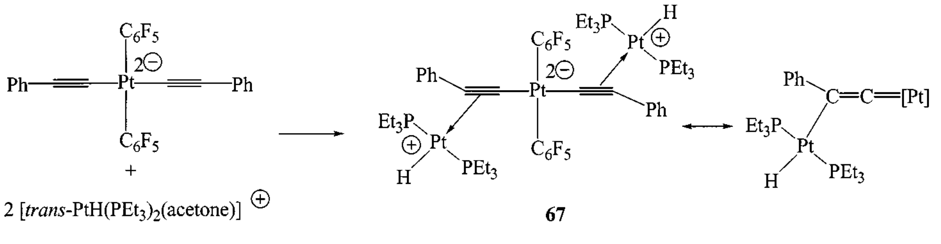
Besides the relative electronegativity of the formally charged fragments tuned by suitable auxiliary ligands, many complexes claimed to be zwitterionic are in fact stabilized by non-zwitterionic π-electron resonance or by partial hapticity. Although these forms have often been regarded



Scheme 34



Scheme 35



Scheme 36

as making only minor contributions, they play the role of a stabilizing force equilibrating the electrostatic destabilization due to charge separation. True zwitterionic complexes, in which the opposite charges are separated by two or more sp^3 carbon atoms (as in **28**, **34**, **35**, **39**, **43**, **56**), are less common, and multinuclear anionic cores and hydrogen-type bonding are found to be present as additional sources of stabilization.

The "zwitterionic metallate" feature may become a fundamental consideration in the design of mixed valence, push-pull or donor–acceptor complexes, for applications in nonlinear optics, molecular electronics, molecular conductivity, etc. Furthermore, just as zwitterionic cationic metal complexes are bringing new perspectives in catalysis, zwitterionic metallates might play a role in governing the activity or selectivity of catalytic reactions through specifically designed hybrid dative-electrostatic interactions in the coordination spheres of reduced metal centers.[56][57]

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