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Organometallic Chemistry

Zwitterionic Relatives of Cationic Platinum Group Metal Complexes: Applications in Stoichiometric and Catalytic σ-Bond Activation

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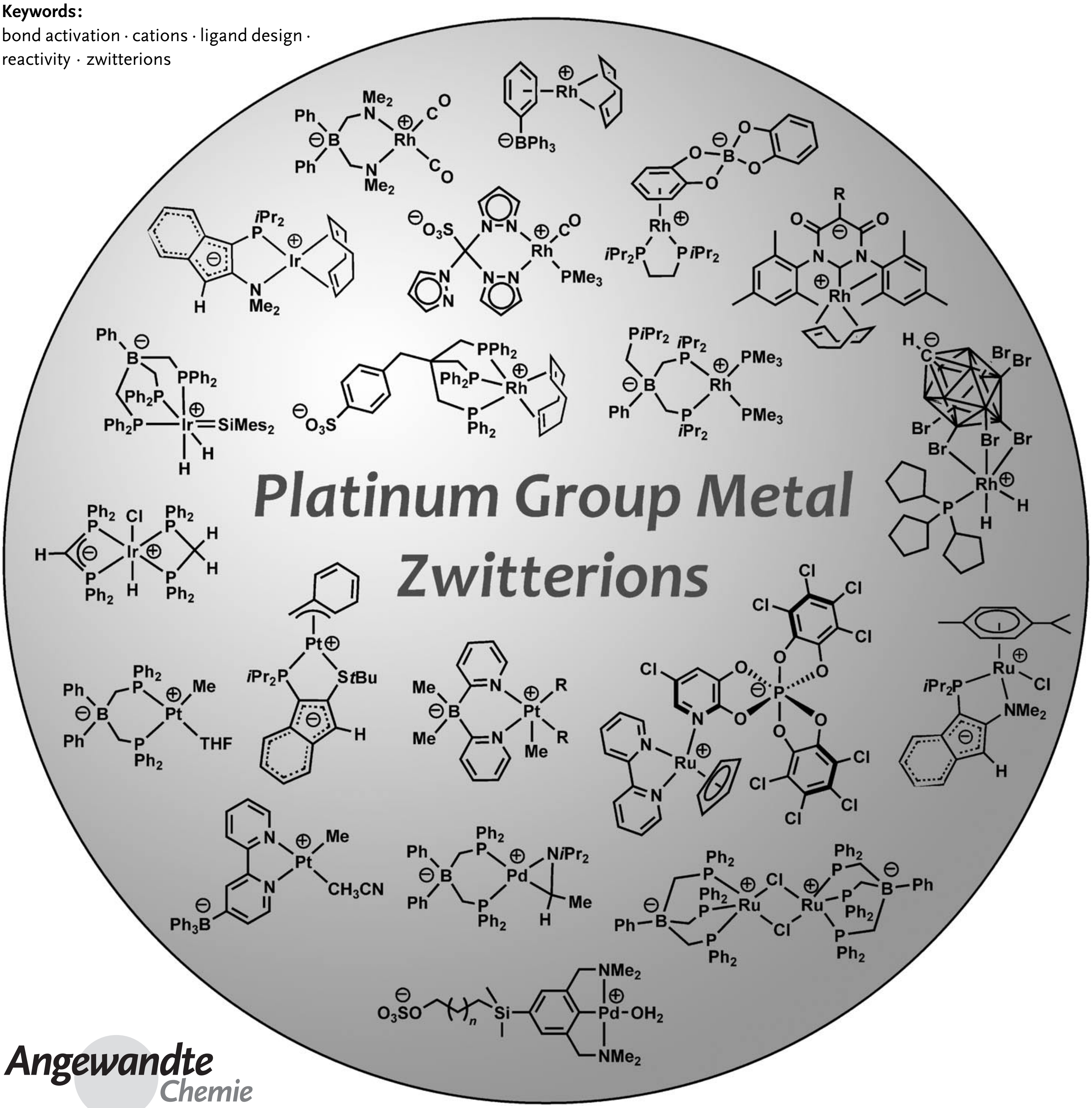

Angewandte Chemie

Zwitterionic platinum group metal complexes that feature formal charge separation between a cationic metal fragment and a negatively charged ancillary ligand combine the desirable reactivity profile of related cationic complexes with the broad solubility and solvent tolerance of neutral species. As such, zwitterionic complexes of this type have emerged as attractive candidates for a diversity of applications, most notably involving the breaking and/or forming of E−H and E−C σ bonds involving a main group element E. Important advances in ancillary ligand design are documented that have enabled the construction of platinum group metal zwitterions. Also summarized are the results of stoichiometric and catalytic investigations in which the reactivity of such zwitterions and their more traditionally employed cationic relatives in σ bond activation chemistry are compared and contrasted.

From the Contents

1. Introduction

Cationic platinum group metal (PGM) complexes figured prominently in the early development of organometallic chemistry, and continue to attract attention owing to the ability of such species to mediate myriad substrate transformations involving the breaking and/or forming of E−H and E−C σ bonds (E = main group element), and often in a manner that cannot be achieved by use of simple neutral PGM complexes. For example, PGM cations provided an entry-point to the important field of catalytic asymmetric hydrogenation,[1] and the ongoing examination of such complexes in this field continues to yield important reactivity breakthroughs.[2] Nonetheless, the inherently polar nature of such discrete salts can limit the range of conditions under which they can be employed; cationic PGM complexes commonly exhibit poor solubility in low-polarity media, and can be rendered inactive in strongly coordinating solvents.[3–5] Furthermore, the systematic design of cationic species is complicated by the fact that the accompanying outer-sphere counteranion can influence the reactivity properties of the complex by ion pairing[6] in a manner that cannot be predicted easily.[7] Zwitterionic (or betaine-like) PGM complexes that feature formal charge separation between a cationic metal fragment and a negatively charged ancillary ligand moiety within an overall neutral molecular framework are attractive alternatives to cations for reactivity studies, including applications in homogeneous catalysis,[8] in that they conceptually merge the appealing reactivity properties of more conventional cationic PGM complexes with the desirable solubility profile and solvent tolerance associated with neutral species. Although it is evident that formal atom charges do not represent true charges within such complexes, a zwitterionic motif that emulates the true charge distribution featured in a cationic complex might indeed be established if formal charge separation between the ancillary ligand and the coordinated cationic PGM fragment can be achieved.

Apart from the reactivity advantages, such as activity and selectivity, that may be brought about by the use of PGM zwitterions in solvents that are not compatible with cationic complexes, the heightened solubility of zwitterions should render these species more amenable to solution-phase characterization, including mechanistic studies. Moreover, the efficient sequestering of the anionic charge in a region of the ancillary ligand that is separated from the metal center should serve to attenuate unwanted ion-pairing in PGM zwitterions versus their cationic relatives, thereby offering an additional control factor in catalyst design. Beyond these practical advantages, head-to-head reactivity studies involving structurally analogous cationic and zwitterionic PGM complexes also provide opportunities to assess the impact of adjusting the electronic properties of a formally cationic PGM center on metal-centered reactivity at a fundamental level, without substantially modifying the steric profile of the reactive metal coordination sphere. Despite the established utility of non-PGM zwitterions in a range of applications (most notably polymerization chemistry[9–12]), rationally prepared PGM zwitterions have emerged only recently, owing in part to the challenge of developing effective ligation strategies for enforcing the requisite formal charge separation. However, recent advances in ancillary ligand design have enabled the preparation of several unique classes of isolable PGM zwitterions that exhibit reactivity patterns in σ-bond activation chemistry that are reminiscent of, or in some cases complementary to, related cationic PGM species.

This Review presents key developments related to the rational design and construction of mononuclear zwitterionic PGM complexes for use in applications involving the breaking and/or forming of E−H and E−C σ bonds, and covers the academic literature up to July 1, 2009. Whereas a Review pertaining to zwitterionic organometallates that feature formal charge separation between an anionic metal fragment and a positively charged ancillary ligand moiety appeared in 2000,[13] no Review describing the development of zwitter-

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ionic analogues of ubiquitous cationic PGM species has appeared in the literature. In an effort to reflect the development of the field, we have chosen to organize our analysis of PGM zwitterions on the basis of the anion-bearing portion of the ancillary ligand, starting with borate-based systems. Emphasis is placed on scrutinizing structural characterization data as a means of assessing the extent to which various ligation strategies succeed in supporting neutral PGM species that adopt a formally zwitterionic ground-state structural motif. From a reactivity perspective, particular attention is given to comparative studies involving structurally analogous cationic and zwitterionic PGM complexes in σ-bond activation chemistry.

2. Borate-Based Ancillary Ligation

Complexes comprising a coordinated BPh_4^- ligand were among the first PGM zwitterions to appear in the literature, and species featuring borate ligation remain the most widely explored class of zwitterionic PGM complexes. In the course of investigating the catalytic utility of $[Rh(nbd)(PPh_3)_2]^+X^-$ (**1**, nbd = η^4-norbornadiene; Figure 1) in hydrogenation chemistry, Osborn and co-workers[14,15] observed a pronounced counteranion effect; whereas variants of **1** containing ClO_4^- or PF_6^- were effective pre-catalysts, the analogous BPh_4^- complex exhibited significantly altered and diminished catalytic performance. The origin of this anomalous behavior was found to be attributable to the propensity of BPh_4^- to form the η^6-coordinated species **2**.[16] Schrock and Osborn[16] recognized that **2** can be regarded as being formally zwitterionic, given the absence of conventional Lewis resonance structures that enable delocalization of the anionic charge on boron into the metal-coordinated phenyl ring. The connectivity in **2** and related rhodium and iridium derivatives (including the η^4-1,5-cyclooctadiene analogue **3**) was proposed on the basis of IR and NMR spectroscopic data,[16] and confirmed through the crystallographic characterization of **4**.[17] In the ensuing years, numerous other mono-, di-, tri-, and tetranuclear Group 8[18–26] and 9[27–36] complexes of BPh_4^- and related phenylborate ligands have been reported. The crystallographically determined M···B distances (> 3.7 Å) in such complexes preclude significant cation–anion interactions, in keeping with a zwitterionic motif.

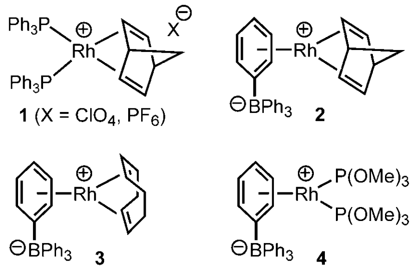
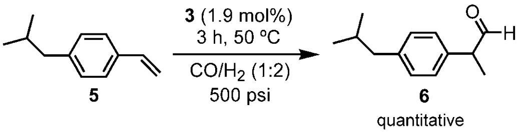


Figure 1. Cationic and phenylborate-ligated zwitterionic rhodium complexes.

Little attention was given to the further use of PGM zwitterions in catalysis until the 1990s, when Alper and co-workers disclosed the utility of Group 9 variants in a wide range of synthetic applications. In their pioneering report,[37] the use of zwitterionic **3** was examined as a pre-catalyst for the hydroformylation of olefins. Compound **3** displayed exceptionally high regioselectivity in the hydroformylation of vinylarenes and vinyl ethers to branched aldehydes; under appropriate conditions, *p*-isobutylstyrene (**5**) afforded quantitatively 2-(4-isobutylphenyl)propanal (**6**; Scheme 1), which can be exploited as a synthetic intermediate en route to the non-steriodal anti-inflammatory agent ibuprofen. Subsequent reports by Alper and co-workers,[38–61] as well as other groups,[62–69] documented the utility of **3** and related phenylborate zwitterions in a diversity of substrate transformations involving the breaking and/or forming of E–H and E–C σ bonds, including (Scheme 2) alkene and alkyne hydroformylation,[37,39,42–44,48,54–56,62,63,69] the germyl- and silylformylation (silylhydroformylation) of alkynes,[46,49,50,53,67,68] the reductive carbonylation of alkenes,[38] the carbonylation and/or cyclization of allylic amines and bromides,[41,47] hydrocarbonylation and silylcarbonylation reactions,[57,60,61,64] the hydroaminomethylation and hydroaminovinylation of alkenes,[58,59,65,66] ketone hydrosilylation,[40] and imine hydrogenation.[51] Compound **3** and related zwitterions have also



Scheme 1. Regioselective hydroformylation of *p*-isobutylstyrene (**5**).

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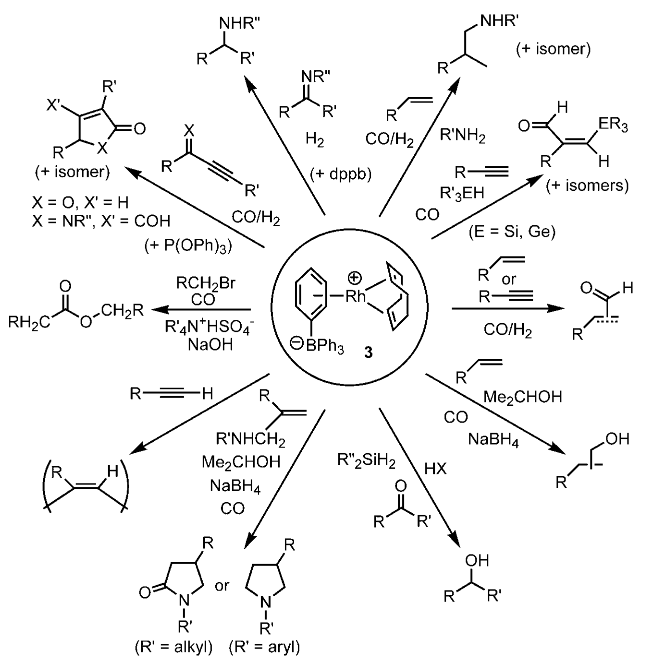
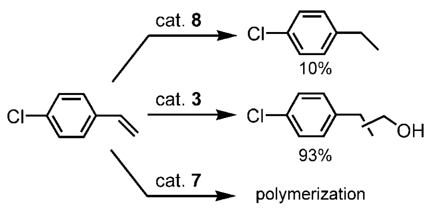


Scheme 2. Summary of substrate transformations catalyzed by zwitterion **3**.

proven to be useful as pre-catalysts in alkyne polymerization chemistry (Scheme 2).[45,70–75]

The performance of zwitterionic **3** was found to be divergent from, or superior to, that of more conventional neutral and cationic complexes in a number of catalytic applications. For example, whereas 95:5 branched selectivity was achieved in the reductive carbonylation of styrene using **3** (1 mol%) as a pre-catalyst, lower selectivity was achieved under similar conditions using either the cationic species $[Rh(cod)(PPh_3)_2]^+BPh_4^-$ (**7**; 64:36) or the neutral complex $[Rh(PPh_3)_3(CO)(H)]$ (**8**; 80:20). Even more dramatic reactivity differences were observed in catalytic transformations employing *p*-chlorostyrene as a substrate (Scheme 3); whereas the use of **3** afforded 93% conversion into the targeted alcohol products in a regioselective manner (3:1), the use of cationic **7** resulted in alkene polymerization, and **8** afforded only 10% conversion into the hydrogenation product *p*-chloroethylbenzene.[38]



Scheme 3. Divergent catalytic performance of neutral (**8**), cationic (**7**), and zwitterionic (**3**) rhodium pre-catalysts under reductive carbonylation conditions (cat. (1 mol%), 100°C, 22 h, $NaBH_4$, CO (500 psi), *i*PrOH) employing *p*-chlorostyrene as a substrate.

Divergent product selectivity has also been observed in the rhodium-mediated silylformylation of terminal alkynes employing zwitterionic **3** and related cationic rhodium pre-catalysts (Scheme 4).[46] Treatment of 1-hexyne with $PhMe_2SiH$ (1.2 equiv) and CO/H_2 (1:1) in the presence of a catalytic amount of **3** afforded **9** in excellent yield. In contrast, analogous reactions employing the cationic pre-catalyst $[Rh(cod)(dppb)]^+BPh_4^-$ (**10**; dppb = 1,4-bis(diphenylphosphino)butane) produced the isomeric alkene **11** preferentially.

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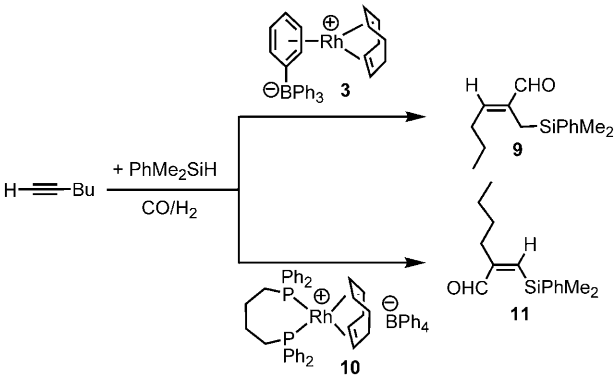
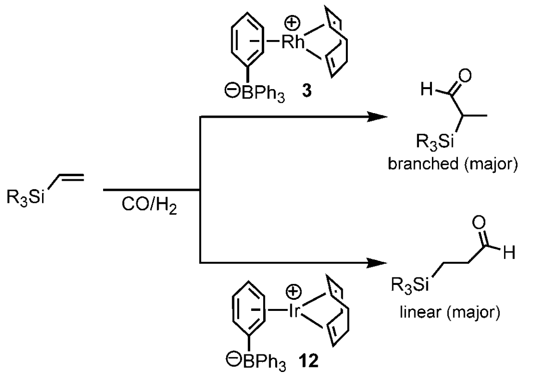


Scheme 4. Divergent product selectivity for cationic (**10**) and zwitterionic (**3**) rhodium pre-catalyst in the silylformylation of terminal alkynes (ca. 1 mol%).

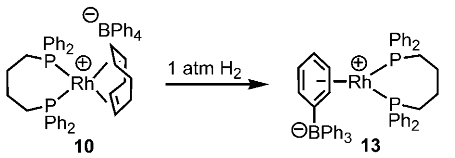
The ability of zwitterionic rhodium and iridium complexes to offer complementary selectivity in hydroformylation has also been demonstrated in studies examining vinylsilane substrates.[44] Whereas the use of the rhodium zwitterion **3** as a pre-catalyst afforded the branched aldehyde selectively in what was the first report of a hydroformylation process leading to an α-silyl aldehyde as the major product, the analogous iridium zwitterion **12** under slightly modified conditions was found to be selective for the linear hydroformylation product (Scheme 5). In examining the ability of $[Rh(cod)_2]^+BF_4^-$ to mediate these transformations, a dramatic influence of solvent on catalytic performance was noted. Unlike the rhodium zwitterion **3**, which performed well in a range of arene, ether, and chlorocarbon solvents, only aromatic solvents proved suitable for use with $[Rh(cod)_2]^+BF_4^-$.

Notwithstanding the utility of **3** and related phenylborate zwitterions as pre-catalysts, several observations bring into question the identity of key reactive intermediates in transformations that employ cationic or zwitterionic pre-catalysts of this type, especially when co-ligands such as dppb are added. These observations include the loss of BPh_4^- from



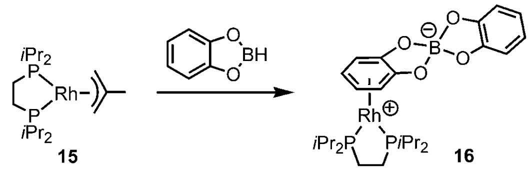
Scheme 5. Differing regioselectivity for rhodium and iridium zwitterions in the hydroformylation of vinylsilanes (ca. 1 mol%).

such zwitterions upon treatment with CO,[70] CO_2,[28] and acetone,[76] and the clean conversion of cationic [Rh(cod)(dppb)]$^+$ BPh_4^- (**10**) into zwitterionic **13** upon exposure to an atmosphere of H_2 (Scheme 6).[52] Indeed, a solution NMR-spectroscopic investigation of **3** in the presence of dppb revealed that zwitterionic [(η^6-$C_6H_5BPh_3$)Rh(diene)$_n$(dppb)$_{1-n}$] and cationic [Rh(diene)$_n$(dppb)$_{2-n}$]$^+$ BPh_4^- species ($n = 0$, 1) coexist and interconvert in solution.[52] These observations are also reflected in the results of catalytic studies. For example, whereas the cationic pre-catalyst [Rh(cod)(PPh$_3$)$_2$]$^+$ BPh_4^- (**7**) and the zwitterion **3** displayed differing amounts of regioselectivity, favoring the branched product in the hydroformylation of allyl acetate, the performance of **3** or **7** in the presence of added dppb under similar conditions proved indistinguishable, favoring almost exclusively the linear hydroformylation product, thereby suggesting that a common catalytic intermediate is accessed in both systems.[42] Similarly, whilst the order of catalytic activity in the hydroformylation of α,β-unsaturated esters was found to be **3** (zwitterionic) > [Rh(cod)(dppb)]$^+$ BF_4^- (**14**; cationic) > [Rh(cod)Cl]$_2$ (neutral), the addition of dppb to each of these pre-catalysts afforded a significantly more active and regioselective catalyst system that did not depend on the nature of the rhodium precursor.[48]

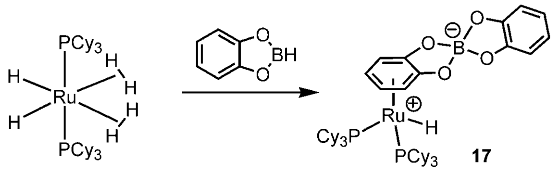


Scheme 6. Transformation of cation **10** into zwitterion **13** upon exposure to H_2.

In the course of documenting the stoichiometric reactivity of catecholatoborane (HBcat) with various rhodium complexes, Marder, Baker and co-workers[77] serendipitously discovered that the zwitterionic complex **16** is formed as the only rhodium-containing product upon treatment of [(η^3-2-methylallyl)Rh(dippe)] (**15**, dippe = 1,2-bis(diisopropylphosphino)ethane) with HBcat (Scheme 7). The convenient preparation of **16** and related rhodium zwitterions were reported subsequently,[78–80] as was the formation and spectroscopic characterization of the rhodium zwitterion **17** (Scheme 8).[81] In keeping with the phenylborate zwitterion **3**, the crystallographically characterized complex **16** can be described as featuring a (dippe)Rh$^+$ moiety that is coordinated in an η^6 fashion to the bis(catecholato)borate anion (Bcat$_2^-$).

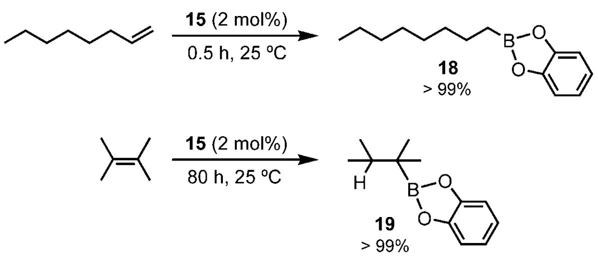


Scheme 7. Formation of the zwitterion **16**.



Scheme 8. Formation of the zwitterion **17**.

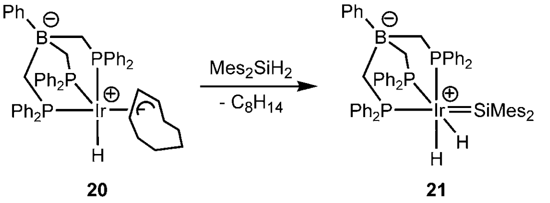
In an initial survey of the rhodium-catalyzed hydroboration of 4-vinylanisole using HBcat, neutral (e.g. **15** or [(PPh$_3$)$_3$RhCl]), cationic (e.g. **14**), and zwitterionic catalysts (such as **16**) all proved equally effective in generating the branched hydroboration product with high (> 99%) regioselectivity; under similar conditions using the dippe analogue of the phenylborate zwitterion **13**, combinations of linear, branched, and hydrogenation products were obtained.[78] However, unlike [Rh(diene)(PR$_3$)$_2$]$^+$ X^- pre-catalysts, including **14**, the hydroboration of 1-octene with HBcat using **15** was found to proceed with complete regiocontrol to afford the terminal alkylboronate ester **18**; complex **15** also proved to be an excellent pre-catalyst for the hydroboration of sterically demanding alkenes, such as 2,3-dimethylbut-2-ene, to afford **19** (Scheme 9).[78] Given the facile conversion of **15** into **16** in the presence of HBcat (Scheme 7), zwitterionic **16** appears to be the resting state of the active hydroboration catalyst. Monitoring by ^{31}P NMR spectroscopy of catalytic hydro-



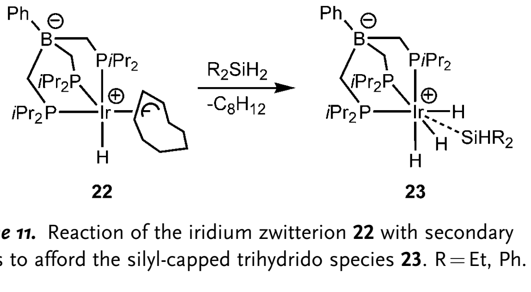
Scheme 9. Alkene hydroboration employing **15** as a pre-catalyst.

boration reactions using pre-catalyst **15** showed that only **16** was present in observable quantities during or upon completion of catalysis, and various reactions employing **16** in place of **15** as a pre-catalyst afforded indistinguishable results. The bis(diphenylphosphino)methane (dppm) analogue of **16** has also proven to be an excellent catalyst for the 1,2-diboration of vinylarenes with B_2cat_2, including the unstrained internal alkenes *cis*- and *trans*-stilbene and *trans*-β-methylstyrene.[79]

Zwitterionic PGM complexes supported by tris(phosphino)borate ligands [RBP_3] were first reported in 1999 by Tilley and co-workers.[82] In contrast to zwitterions featuring BPh_4^- or $Bcat_2^-$ that rely on η^6-arene interactions to bind a formally cationic PGM fragment, the three M−P linkages featured in κ^3-[RBP_3]ML_n complexes serve to anchor the borate ligand to the metal, thereby affording more robust zwitterionic structures. The crystallographically determined M···B distances in ruthenium,[83,84] rhodium and iridium,[82,83,85–87] and platinum[88] zwitterions featuring κ^3-[RBP_3] ligation (> 3.6 Å) suggest that metal-borate interactions are not significant. Preliminary evidence of the capacity of [RBP_3] ligands to support reactive PGM zwitterions was demonstrated by the reaction of **20** with dimesitylsilane (Mes_2SiH_2) to give [[$PhBP_3$]$(H)_2Ir{=}SiMes_2$] **21** with loss of cyclooctene—the first example of metal-mediated silylene extrusion from an organosilane by double geminal Si−H bond activation (Scheme 10).[82] Subsequent studies confirmed the ability of **20** to participate in analogous double geminal Si−H and Ge−H bond activation processes with other secondary silanes (for example with R = Me, Et, or Ph), primary silanes (R = Mes or 2,4,6-triisopropylphenyl), and Mes_2GeH_2.[86] However, the course of such E−H bond activation chemistry was found to be sensitive to the nature of the substituents at phosphorus within the [RBP_3] ligand; analogous reactions of the di(isopropyl)phosphino complex **22** with Et_2SiH_2 or Ph_2SiH_2 each afforded the corresponding silyl-capped trihydrido species **23** with loss of 1,3-cyclooctadiene (Scheme 11).[87]

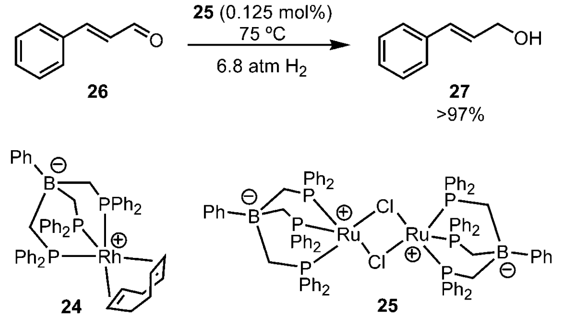


Scheme 10. Silylene extrusion by the iridium zwitterion **20**.



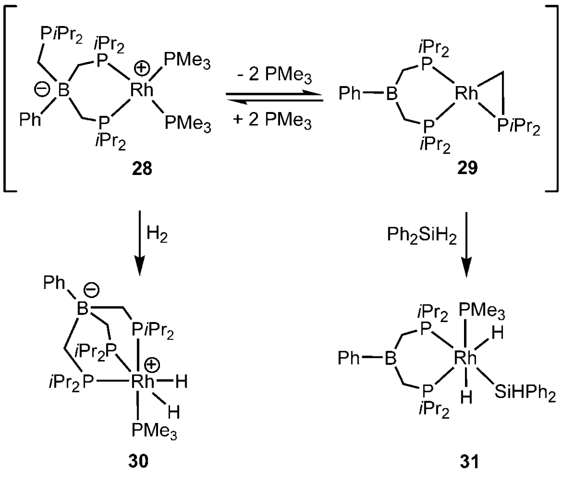
Scheme 11. Reaction of the iridium zwitterion **22** with secondary silanes to afford the silyl-capped trihydrido species **23**. R = Et, Ph.

The utility of [RBP_3]-ligated PGM species in catalysis remained undocumented until the use of zwitterions **24** and **25** as pre-catalysts for the selective hydrogenation of α,β-unsaturated substrates was reported in 2009.[83] Both **24** and **25** proved to be particularly efficient catalysts for the selective hydrogenation of cinnamaldehyde (**26**) to the corresponding allyl alcohol **27**, with the ruthenium zwitterion **25** being one of the most efficient catalysts known for this transformation (Scheme 12).



Scheme 12. Zwitterion-catalyzed chemoselective hydrogenation of cinnamaldehyde (**26**).

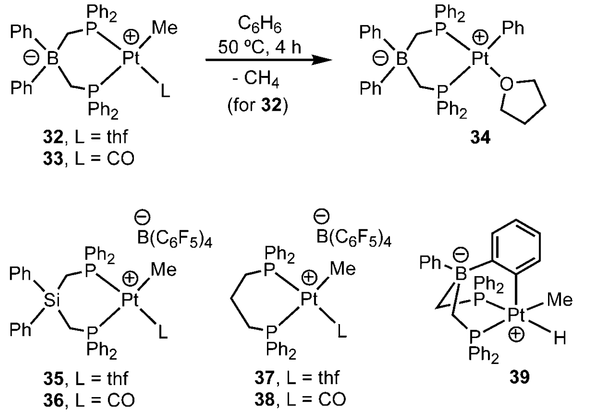
Notwithstanding the aforementioned stoichiometric and catalytic E−H bond activation chemistry exhibited by PGM zwitterions featuring [RBP_3] ligation (Scheme 10–12), ancillary ligand degradation pathways leading to non-zwitterionic species have been identified. Although variable-temperature NMR experiments do not support κ^2-κ^3 interconversion within the square-planar complex **28**, at elevated temperatures this zwitterionic species was found to engage in an unusual dynamic equilibrium involving dissociation of the PMe_3 ligands and reversible migration of a CH_2PiPr_2 fragment from B to Rh (Scheme 13).[87] Compound **29**, the non-zwitterionic PMe_3-free product of this migration, was prepared independently and characterized crystallographically. Although detailed mechanistic data are still lacking, reactivity



Scheme 13. Interconversion of **28** and **29**, and reactivity with H_2 and Ph_2SiH_2 to afford **30** and **31**.

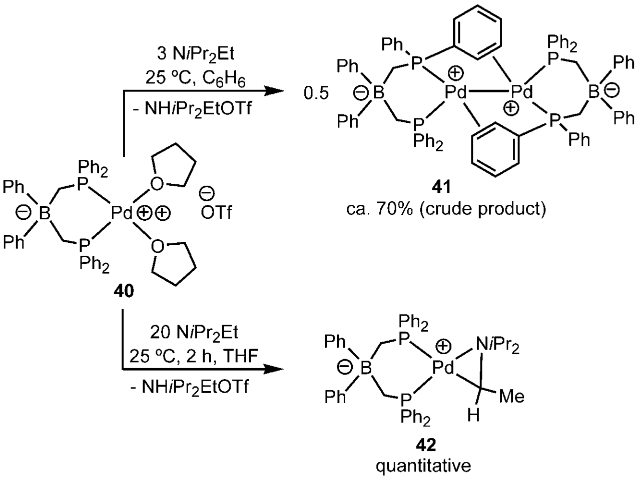
studies suggest that both components of this equilibrium mixture can be viewed as engaging in σ-bond activation. For example, **30** can be envisioned as arising from H_2 addition to **28**, and the formation of **31** may result from the addition of Ph_2SiH_2 to **29** (Scheme 13).[87]

Peters and co-workers have developed zwitterionic PGM complexes supported by homobidentate κ^2-[R_2BL_2] (L = P or N) ligands, which have found application in a range of stoichiometric and catalytic transformations. The preliminary report on such systems appeared in 2001, in which the ability of the crystallographically characterized zwitterionic Pt–Me complex **32** (Pt···B > 3.9 Å) to activate the C–H bonds in benzene (affording the Pt–Ph species **34**) and toluene was presented (Scheme 14).[89] The structurally related cationic complexes **35**, which feature the neutral [Ph_2SiP_2] ligand, and **37** were also shown to undergo C–H bond activation with benzene to afford the corresponding Pt–Ph complexes.[90] Solution-IR spectroscopy data for the Pt–CO complexes **33**, **36**, and **38** ($\tilde{\nu}_{CO}$ = 2094, 2118, and 2118 cm^{-1}, respectively; in CH_2Cl_2) suggest that the platinum center in the zwitterion **33** is more electron rich than in the structurally related cations **36** and **38**; the more electron-releasing nature of the anionic [Ph_2BP_2] ligand may contribute to the enhanced rate of C–H bond activation observed for **32** relative to **35** and **37**. Further studies revealed important differences between these cationic and zwitterionic systems with respect to the mechanism of C–H bond activation.[90] Whereas CH_4 is the predominant isotopologue of methane that is evolved during the thermolysis of zwitterionic **32** in C_6D_6, under similar conditions employing the cations **35** or **37**, CH_3D is the dominant by-product; markedly different primary kinetic isotope effects ($k(C_6H_6)/k(C_6D_6)$ = 1.26 (**32**), 6.52 (**35**), ca. 6 (**37**)) were also observed. In contrast to the associative mechanism of THF self-exchange that is apparent from kinetic data obtained for the cations **35** and **37**, the mechanism of THF self-exchange in zwitterionic **32** is ligand-assisted (or dissociative). It is reasonable to infer that these mechanistic differences hold true for the displacement of THF by benzene in benzene solution, en route to C–H bond activation. Furthermore, whereas ancillary ligand metalation appears to be insignificant for **35** and **37**, such processes involving P–Ph and B–Ph fragments in **32** (leading to an observable intermediate of type **39** or **39**·THF, as well as the evolution of CH_4 rather than CH_3D during thermolysis in C_6D_6) figure prominently during the course of benzene C–H bond activation chemistry.[90]



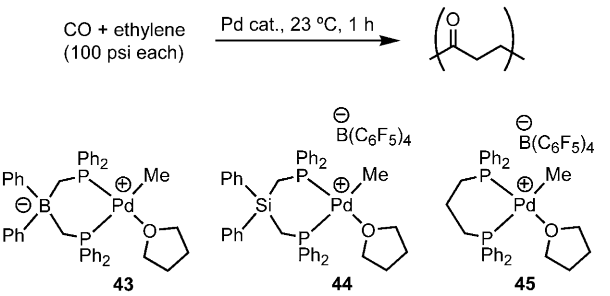
Scheme 14. Cationic and zwitterionic platinum complexes, including benzene C–H bond activation by the platinum zwitterion **32**, leading to **34**.

In an effort to extend such arene C–H bond activation chemistry to related zwitterionic palladium complexes, the behavior of the zwittercation **40** in benzene at room temperature in the presence of N*i*Pr_2Et (three equivalents) was examined by Peters and co-workers (Scheme 15).[91] Whilst the dinuclear complex **41** was obtained as the major product under these conditions, replacing benzene with THF as the solvent and using 20 equivalents of N*i*Pr_2Et resulted in the clean formation of the iminium adduct **42**, which arises from C–H bond cleavage in N*i*Pr_2Et by way of β-hydride elimination (Scheme 15). In this manner, compound **40** was capable of cyclometalating a variety of trialkylamines. In contrast, [[Ph_2SiP_2]Pd(OTf)$_2$] reacted in THF in the presence of only three equivalents of N*i*Pr_2Et to afford the dinuclear dicationic species [([Ph_2SiP_2]Pd)$_2$]$^{2+}$(OTf$^-$)$_2$ as the major product, in analogy to **41**.[91] Given the more electron-releasing nature of anionic [Ph_2BP_2] versus neutral [Ph_2SiP_2], such divergent reactivity may be attributed to the heightened ability of the [Ph_2BP_2]Pd fragment in **42** to stabilize the coordinated iminium ligand by π-back donation. In a related study, the ability of zwitterionic [Ph_2BP_2]Pd species **43** to catalyze the co-polymerization of carbon monoxide and ethylene in a manner similar to the structurally related cationic species **44** and **45** was demonstrated (Scheme 16).[92]



Scheme 15. Probing the reactivity of the palladium zwittercation **40** with N*i*Pr_2Et.

The synthesis, structural characterization, and catalytic utility of zwitterionic rhodium complexes supported by anionic [Ph_2BP_2] or [Ph_2BN_2] ligands (for example **46**–**51**; Figure 2) have been reported by Peters and co-workers.[93,94] In keeping with previously characterized PGM zwitterions of this type, crystallographic data obtained for **46**–**48** and **51** revealed no inter- or intramolecular ion-pairing interactions,



Scheme 16. Ethylene/CO copolymerization catalyzed by cationic and zwitterionic palladium complexes.

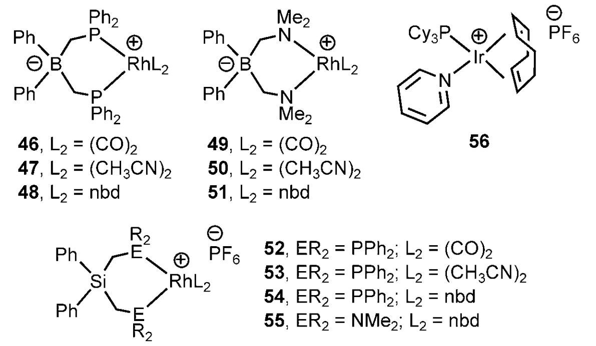
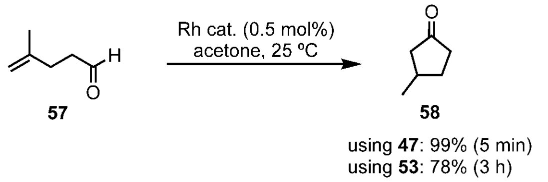
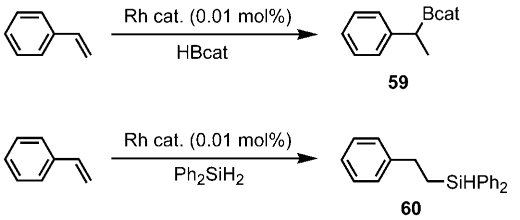


Figure 2. Cationic Group 9 complexes and related rhodium zwitterions supported by [Ph_2BP_2] or [Ph_2BN_2] ligands.

and the observed Rh···B distances (>3.6 Å) confirmed that the borate fragment is spatially separated from the rhodium center. The symmetric and antisymmetric carbonyl vibrations in the IR spectrum of **46** (2080 and 2029 cm^{-1}; in CH_2Cl_2) appear at lower frequency than those of the structurally related cation **52**, thus pointing to a more electron-rich rhodium center in the zwitterion. Nonetheless, such zwitterions displayed catalytic profiles for E−H bond additions to alkenes (E = H, B, C, and Si) that are reminiscent of, and in some cases superior to, more conventional electrophilic $[Rh(solv)_2(PR_3)_2]^+X^-$ species.[3,4] In a survey of rhodium-catalyzed styrene hydrogenation, the zwitterions **48** and **51** out-performed their cationic counterparts (**54** and **55**) in terms of activity; perhaps surprisingly, the [Ph_2BN_2]-ligated zwitterion **51** was the most active of the catalysts surveyed.[93] However, despite the well-established utility of P,N-ligated rhodium and iridium cations including Crabtree's catalyst **56**[5] in alkene hydrogenation,[2] PGM complexes featuring heterobidentate borato P,N-ligands have yet to be reported, and zwitterionic iridium derivatives of [R_2BP_2] or [R_2BN_2] are limited to [[Ph_2BP_2]Ir(tpy)$_2$] (tpy = 2-*p*-tolylpyridyl), which was prepared in the context of an investigation of ligand effects on the excited-state properties of iridium(III) complexes.[95]



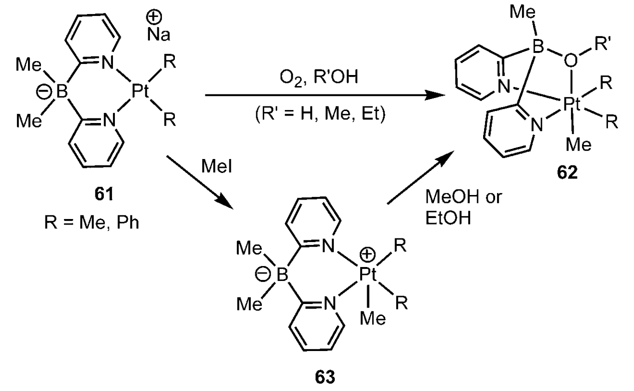
Scheme 17. Rhodium-mediated hydroacylation of **57** employing zwitterionic **47** and cationic **53** as pre-catalysts.



Scheme 18. Rhodium-mediated regioselective hydroboration and hydrosilylation of styrene.

In surveying the rhodium-mediated hydroacylation of 4-methyl-4-pentenal (**57**) to 3-methylcyclopentanone (**58**) in acetone (Scheme 17), zwitterionic pre-catalysts provided an advantage over cationic pre-catalysts in maintaining excellent activity in the presence of both high- and low-polarity solvents. For example, in employing zwitterionic **47** as a pre-catalyst, 99% conversion into **58** was achieved after 5 min, whereas only 78% conversion was attained after 3 h when using **53**; the turnover frequency (TOF) of **47** (2400 h^{-1}) in this catalysis was also found to be 40 times greater than that achieved by use of analogous cationic pre-catalysts, including **53**. Furthermore, whilst the catalytic performance of **47** was unaltered in benzene, THF, or acetonitrile, significantly diminished activity was noted for **53** under similar conditions. Such divergent reactivity behavior may be attributable to the poor solubility of cationic species in low-polarity media, such as benzene, as well as solvent inhibition by more polar solvents, such as acetonitrile.[93] A comparison of the performance of cationic and zwitterionic rhodium pre-catalysts, including **47**, **50**, **53**, and **55**, in the hydroboration and hydrosilylation of styrene (using HBcat in THF, and Ph_2SiH_2 in acetone, respectively) was also examined (Scheme 18). In all cases, the [Ph_2SiN_2]-ligated cation **55** performed poorly, providing inconsistent results owing to a propensity to form rhodium(0); otherwise, in all the reactions, only **59** or **60** were obtained as products. In the absence of CH_3CN, the cationic pre-catalysts surveyed (including **53**) were found to be three to four times more active than the zwitterions **47** and **50**. However, whereas the catalytic activity of these rhodium cations was completely inhibited upon addition of appreciable quantities of CH_3CN, the zwitterions **47** and **50** proved tolerant to these conditions, even when using up to 50% by volume CH_3CN as the reaction medium.[93]

Vedernikov and co-workers have observed that exposure of the anionic borate complexes **61** to an O_2/R′OH mixture (R′ = H, Me, or Et) in benzene or THF affords the corresponding platinum(IV) species **62** (Scheme 19).[96] This methyl migration process was proposed to occur as an electrophilic substitution at one of the B−CH_3 sites by a five-coordinate platinum(IV) zwitterion, accompanied by nucleophilic attack of solvent at boron. To probe the



Scheme 19. Conversion of **61** into **62** via the zwitterionic platinum(IV) intermediate **63**.

feasibility of this reaction pathway and the role of the oxidant, it was demonstrated that the conversion of **61** into zwitterionic **63** proceeds cleanly upon treatment with MeI, and in turn these zwitterionic intermediates are transformed into **62** upon exposure to MeOH or EtOH. The reversibility of such methyl migration processes, and also the ability of phenyl transfer between boron and platinum(IV) to occur in both directions, has also been demonstrated.[97]

Several reports detailing the synthesis and characterization of zwitterionic PGM complexes supported by pnictogen-based donor ligands that feature pendant BPh_3 groups have appeared in the literature, including the platinum zwitterantions **64**,[98] the half-sandwich ruthenium complexes **65**,[99] and the bipyridylborate platinum species **66**[100] (Figure 3); however, no accompanying reactivity studies were carried out.

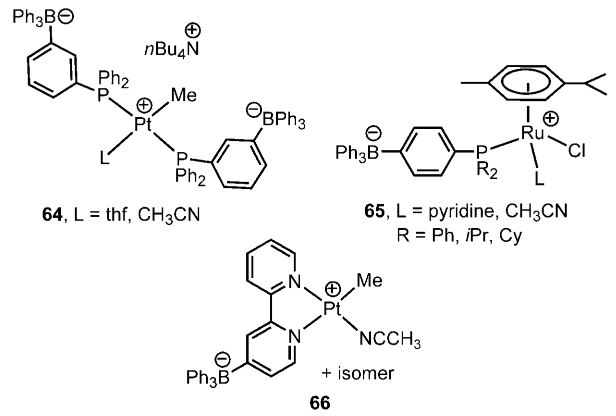


Figure 3. Selected PGM zwitterions featuring pendant BPh_3 fragments.

3. Carbanion-Based Ancillary Ligation

Donor-substituted indenides developed by Stradiotto and co-workers are the most widely explored class of non-borate ancillary ligands for use in preparing PGM zwitterions. In contrast to the η^5 binding of metal fragments that is traditionally observed in indenyl–metal chemistry, these zwitterions can be viewed as comprising a formally cationic PGM fragment whose charge is counterbalanced by a sequestered, uncoordinated 10π-electron indenide unit that is built into the backbone of a bidentate ancillary ligand. Apart from offering an alternative approach to the preparation of PGM zwitterions that is complementary to borate ligation, the convenience of employing a single indene-based ligand precursor in the synthesis of cationic and zwitterionic species has advantages over alternative strategies that require the preparation of distinct ligands for supporting cationic and zwitterionic complexes.

The square-planar rhodium and iridium complexes **67** and **68** (Figure 4) were the first zwitterions of this type to be reported;[101,102] they are also the first heterobidentate Group 9 zwitterions to appear in the literature. A comparative crystallographic analysis revealed that the M—P and M—N contacts within **67** and **68** and the related cations **69** and **70** (that is, the conjugate acids of **67** and **68**) differ only modestly, thereby confirming the nearly isosteric relationship between anionic P,N indenide and neutral P,N indene ligation with respect to the metal coordination sphere.[103] However, whilst pronounced bond-length alternation is observed within the indene portion of the P,N ligand in each of these Group 9 cations, the P,N indenide moiety within each of **67** and **68** exhibits a more delocalized structure that is consistent with a Hückel aromatic framework. At first glance, **67** and **68** lack conventional resonance contributors that place the anionic charge onto either of the pnictogen donor groups; nonetheless, the somewhat short P—C3 and C1—C2 distances (Figure 4) suggest that non-zwitterionic resonance structures (**67a** and **68a**) may also figure prominently in these Group 9 zwitterions.[103] Such structural patterns have also been observed in a range of other crystallographically characterized PGM zwitterions supported by P,N indenide and related ligands.[104–112] In the case of **67**, it was also demonstrated that exclusion of either of the pnictogen donors affords more conventional η^5-indenylrhodium species featuring a pendant donor fragment (**71** and **72**).[113]

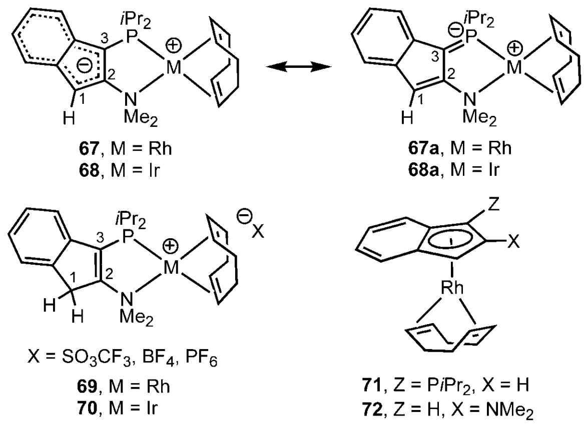
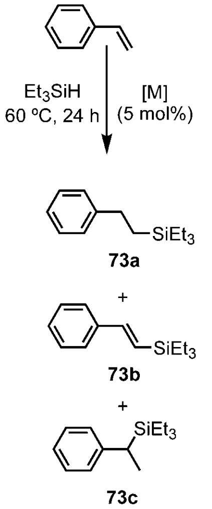


Figure 4. Neutral, cationic, and zwitterionic Group 9 derivatives of donor-substituted indenes. Selected bond lengths [Å]: P—C3: **67** 1.758(2), **68** 1.755(2), **69** 1.809(4), **70** 1.807(2)–1.812(5); C1—C2: **67** 1.386(3), **68** 1.381(3), **69** 1.508(6), **70** 1.491(7)–1.519(7).

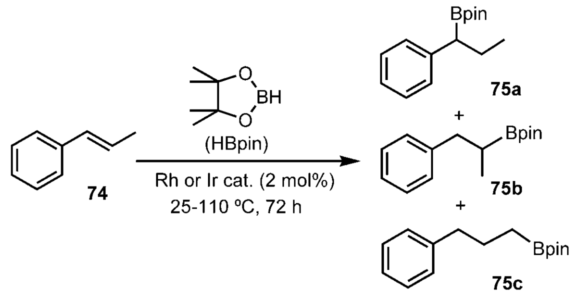
Despite the apparently similar metal coordination spheres featured in these structurally related Group 9 cation/zwitterion pairs, catalytic studies examining (transfer) hydrogenation,[102,103,114] hydrosilylation,[101,103] and hydroboration[115] highlighted important reactivity differences within and between these classes of complexes. Notably, these studies employing **68** represent rare examples of the use of an iridium zwitterion in catalytic applications.[44,116] Whilst the PF_6^- salt of **70** proved to be superior to the zwitterions **67** and **68** as a pre-catalyst for styrene hydrogenation in CH_2Cl_2 or THF, similarly high conversions into ethylbenzene were achieved by use of **67** as a pre-catalyst in benzene—a solvent in which cationic **69** and **70** exhibit poor solubility.[102,103] The catalytic utility of **67** and **68** was demonstrated further in hydrosilylation and hydroboration reactions, wherein these zwitterionic complexes were observed to meet or exceed the performance of their cationic relatives. Although nearly quantitative silane conversions were obtained by use of either **67** or **68** as a pre-catalyst for the addition of triethylsilane to styrene (Scheme 20), these zwitterions were found to exhibit remarkably high, but divergent, selectivity; the use of **67** in THF afforded the terminal dehydrogenative silylation product **73b** preferentially, whereas the use of **68** as a pre-catalyst in 1,2-dichloroethane (DCE) afforded the terminal addition product **73a** exclusively.[101,103] Under similar conditions, using the PF_6^- salt of either **69** in THF or **70** in DCE, conversions of only 37% (**69**) and 66% (**70**) were achieved. Although high conversions were also achieved in this transformation by use of Crabtree's catalyst (**56**, Figure 2), poor selectivities resulted (**73a**/**73b**/**73c** 51:40:7).[103]



	[M] = **67** in THF	[M] = **68** in DCE	[M] = **56** in DCE
73a	10%	99%	51%
73b	90%	0%	40%
73c	0%	0%	7%

Scheme 20. Hydrosilylation of styrene employing rhodium (**67**) and iridium (**68**) zwitterions along with Crabtree's catalyst (**56**).

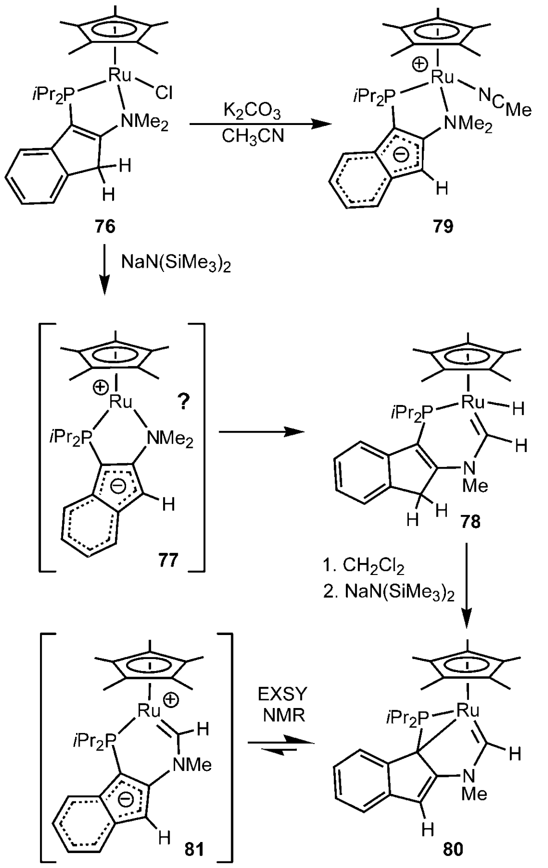
In examining the catalytic hydroboration of 1-phenylpropene (**74**) with pinacolborane (HBpin), the rhodium zwitterion **67** provided **75a** exclusively, whereas the PF_6^- salt of cationic **69** afforded an 80:20 mixture of **75a** and **75b** (Scheme 21). Whilst the iridium zwitterion **68** afforded an alternative product (**75c**) quantitatively, corresponding to net double-bond migration in **74** followed by terminal borane addition, the performance of the PF_6^- salt of **70** proved to be indistinguishable under similar experimental conditions.[115] Overall, when catalytic activity, selectivity, and solvent compatibility are considered, these Group 9 cations and zwitterions (**67**–**70**) appear to constitute a complementary family of pre-catalysts for the addition of E–H bonds (E = H, B, Si) to unsaturated substrates.



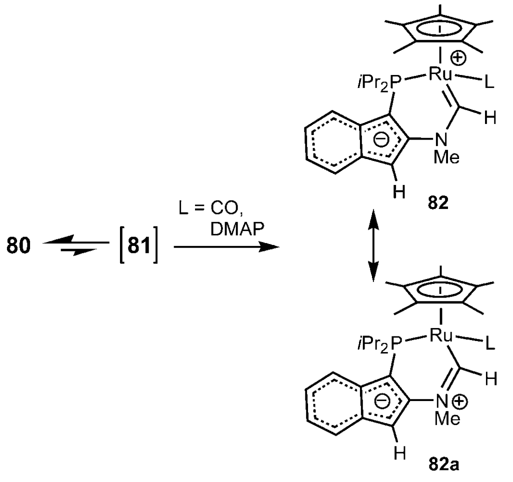
Scheme 21. Hydroboration of 1-phenylpropene (**74**).

Inspired by the rich stoichiometric and catalytic reactivity exhibited by coordinatively unsaturated [Cp^*RuL_n] complexes, the Stradiotto group sought to extend the P,N indenide ligation featured in **67** and **68** to Cp*Ru systems by dehydrohalogenation of **76** with $NaN(SiMe_3)_2$ (Cp* = η^5-pentamethylcyclopentadienyl; Scheme 22).[104,105] This reaction afforded the hydridocarbene **78**, possibly via the unobserved target zwitterion **77** as an intermediate. The formation of **78** corresponds to net double geminal C–H bond activation of a NMe group in putative intermediate **77**, with accompanying transfer of a proton to the indenide backbone. Support for the viability of **77** was obtained through the preparation of the isolable zwitterion **79** (i.e., the CH_3CN adduct of **77**). Treatment of the Ru–H species **78** with dichloromethane, followed by dehydrohalogenation of the intermediate Ru–Cl complex afforded the crystallographically characterized compound **80**; on the basis of EXSY NMR data, this complex was shown to provide access to the zwitterion **81**, by way of a facile and reversible Ru–C(sp^3) bond cleavage process.[109,110] Exposure of **80** to an atmosphere of CO or one equivalent of 4-dimethylaminopyridine (DMAP) afforded the corresponding zwitterionic adducts **82** (i.e., **81**·L; Scheme 23). Crystallographic data obtained for the DMAP adduct indicate that resonance structures **82** and **82a** both should be considered when describing the electronic structure of this complex.[110]

The ability of **80** to serve as a source of the reactive zwitterion **81** in situ was demonstrated in stoichiometric transformations involving a range of small-molecule substrates. Exposure of **80** to an atmosphere of H_2 or excess *i*PrOH regenerated the hydridocarbene **78**. Notably, this observation suggests that the Lewis acidic metal center and the Lewis basic indenide unit in **81** and related zwitterions have the capacity to cooperate in the activation of substrates (Scheme 24). Treatment of **80** with Ph_3SiH or Ph_2SiH_2 allowed the observation of the corresponding zwitterionic product (**83** or **84**, respectively) arising from Si–H oxidative addition to ruthenium in the putative zwitterion **81**. Whereas the trans-

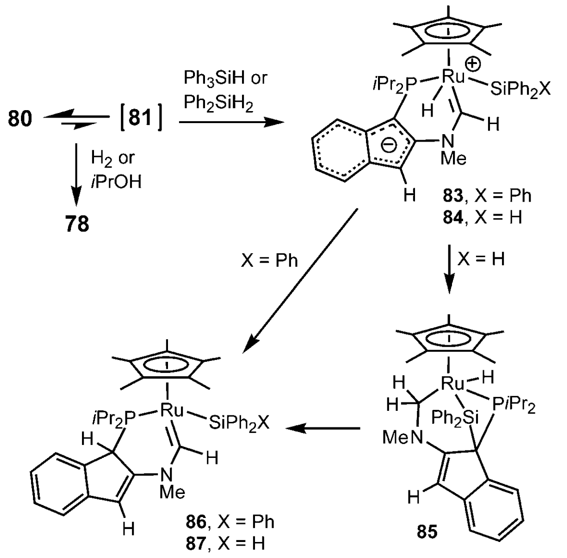


Scheme 22. Double geminal C–H bond activation in **77** to give **78**, and facile Ru–C bond cleavage in **80** to afford **81**.

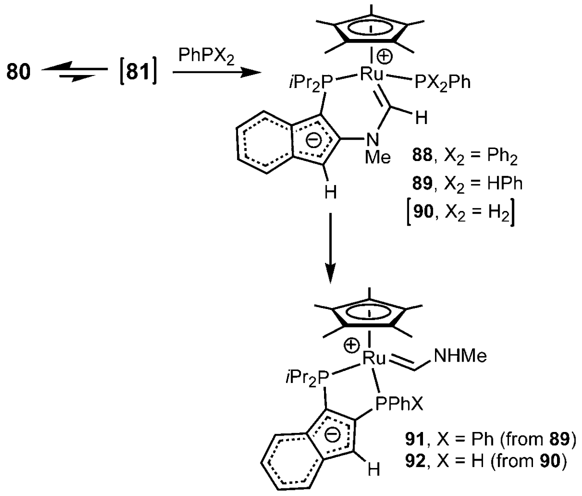


Scheme 23. Trapping of the putative zwitterion **81** with CO and DMAP.

formation of the Ph$_3$SiH addition product **83** into **86** occurred without formation of observable intermediates by ^{31}P NMR, the rearrangement of **84** into **87** proceeded via the isolable complex **85**.[110] In keeping with the formation of **82** upon treatment of **80** with CO or DMAP (Scheme 23), the addition of PPh$_3$ or Ph$_2$PH to **80** afforded the corresponding zwitterionic adducts **88** and **89** (Scheme 25). In the case of **89**, continued monitoring of the reaction allowed for the quantitative conversion into the P,P-indenide complex **91** to be observed. In examining the reaction of PhPH$_2$ with **80**, the adduct **90** was not observed en route to the zwitterionic P,P-ligated complex **92**.

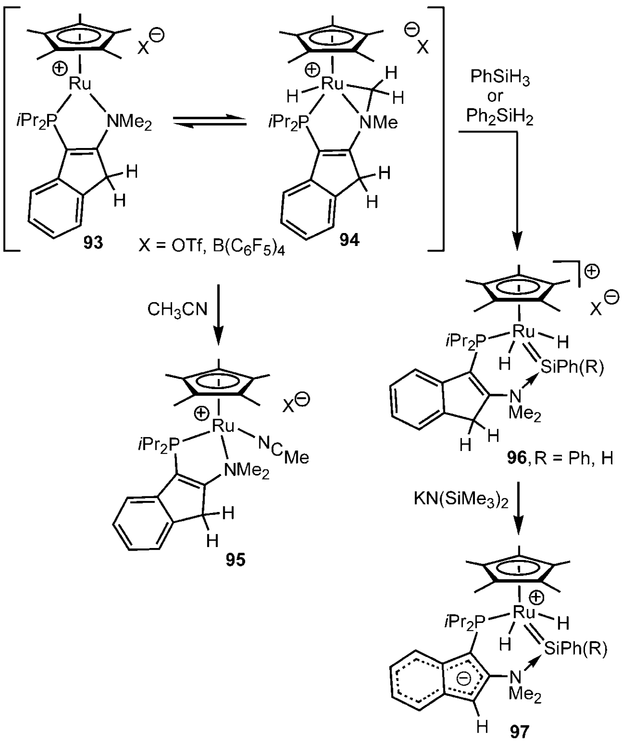


Scheme 24. Reaction of the putative zwitterion **81** with silanes.



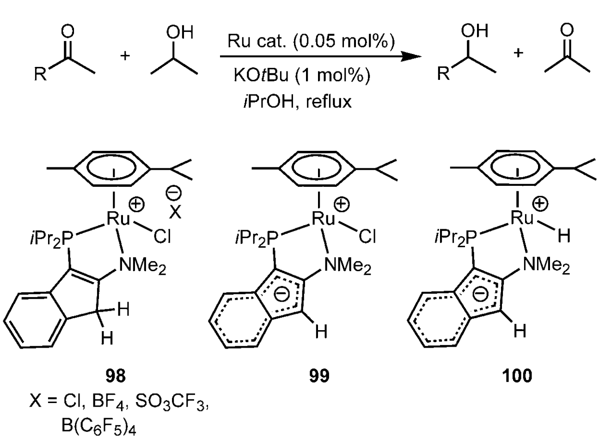
Scheme 25. Reaction of the putative zwitterion **81** with phosphines.

The cationic, coordinatively unsaturated ruthenium center of complex **93** (the conjugate acid of **77**) reversibly inserts into C–H bonds of the pendant NMe group, as evidenced by solution NMR data and the crystallographic characterization of **94** (Scheme 26). Further support for the involvement of **93** was obtained by the isolation of the acetonitrile adduct **95**.[104,105] Treatment of cationic **93** with PhSiH$_3$ or Ph$_2$SiH$_2$ afforded the base-stabilized Ru=Si complexes **96**, which result from double geminal Si–H bond activation of the organosilane. The structurally analogous zwitterionic Ru=Si complexes **97** were prepared by treatment of **96** with KN(SiMe$_3$)$_2$.[108]



Scheme 26. Reaction of **93/94** with acetonitrile and silanes.

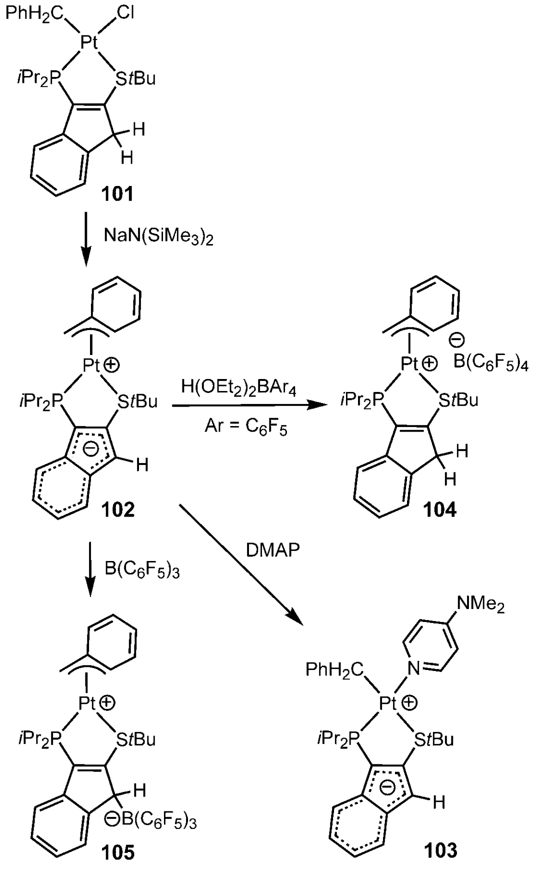
Divergent catalytic performance was observed in the course of a comparative catalytic investigation to probe the ability of the structurally analogous cationic and zwitterionic (η^6-arene)Ru complexes **98** and **99** to mediate the transfer hydrogenation of ketones under basic conditions and employing *i*PrOH as an H_2 donor solvent (Scheme 27).[107] In a preliminary test reaction employing acetophenone (R = Ph in Scheme 27), the cation **98** exhibited only modest activity, with final conversions into 1-phenylethanol in the range of 4–23 %. In stark contrast, the zwitterion **99** afforded 99 % conversion into 1-phenylethanol after only five minutes. The pre-catalyst **99** was shown to provide near quantitative conversions for a diversity of alkyl and/or aryl ketone substrates at low loadings and with TOF values (up to 220000 h^{-1}), which are among the highest reported for ketone transfer hydrogenation. Given that the preponderance of experimental evidence points to Ru–H species being the active catalysts formed in situ from Ru–Cl pre-catalysts during the course of ketone transfer hydrogenation reactions conducted in basic *i*PrOH, it is surprising that the rationally prepared zwitterion **100** (0.05 or 0.2 mol %) is completely inactive. In fact, the formation of **100** has been shown to be a catalyst deactivation pathway in ketone transfer hydrogenation reactions employing **98** or **99** as pre-catalysts.[107] Nonetheless, such an observation does not rule out the involvement of alternative hydrido species as active catalysts in reactions employing **99**, including those arising by intramolecular C–H bond activation, as was observed for **77** (Scheme 22) and **93** (Scheme 26). Whilst in a related investigation little difference was observed between the performance of the cationic and zwitterionic iridium pre-catalysts **68** and **70** (Figure 4) in the transfer hydrogenation of acetophenone (2 h, 0.1 mol % Ir, 93–98 %; 37000–47000 h^{-1}), these complexes out-performed Crabtree's catalyst (**56**, Figure 2), which afforded only 29 % conversion under similar experimental conditions.[114] The utility of neutral, cationic, and zwitterionic Cp*Ru and (η^6-arene)Ru complexes, such as **76**, **79**, **93/94**, **95**, **98**, and **99**, as pre-catalysts for the atom transfer radical addition of chlorocarbons to alkenes has also been examined.[117]



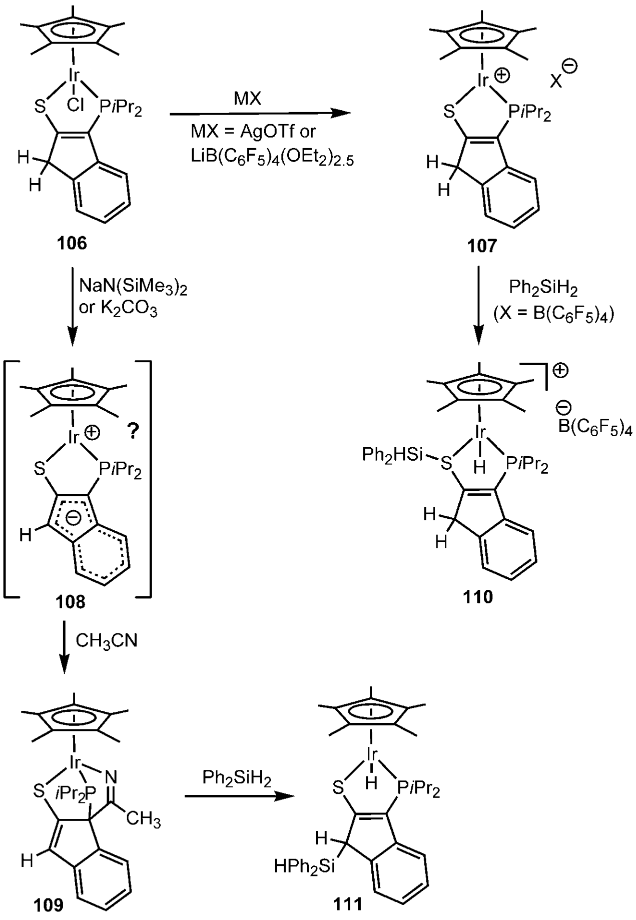
Scheme 27. Cationic (**98**) and zwitterionic (**99**) ruthenium complexes as pre-catalysts in the transfer hydrogenation of ketones.

Further to PGM zwitterions featuring P,N- and P,P-indenide ligation, some related P,S complexes have also been reported.[112,118] Dehydrohalogenation of **101** afforded the (η^3-benzyl)Pt zwitterion **102**, which was shown to react with DMAP to give the adduct **103** (Scheme 28). Whilst halide abstraction from **101** was not an effective route to the structurally related cation **104**, HX addition to the zwitterionic conjugate base **102** provided access to **104**. The versatility of the P,S-indenide ligation featured in **102** was further demonstrated by the direct transformation of carbanion-based zwitterion **102** into the borate-based zwitterion **105** upon treatment with $B(C_6F_5)_3$.

Chloride abstraction from the phosphinothiolate precursor **106** cleanly provided the cationic species **107** (Scheme 29). Efforts to prepare the corresponding zwitterion **108** by dehydrohalogenation of **106** produced a green solid that could not be unequivocally identified. However, the ability of this material to serve as a functional source of **108** was confirmed by the formation of the unusual bridging adduct **109** upon treatment with CH_3CN. Whereas exposure of the $B(C_6F_5)_4^-$ salt of **107** to Ph_2SiH_2 resulted in net Si–H addition across the S–Ir bond to afford **110**, treatment of **109** with Ph_2SiH_2 resulted in the loss of CH_3CN, along with the production of **111**. The formation of **111** corresponds to heterolytic Si–H bond activation involving net addition of H^- and Ph_2HSi^+ fragments to iridium and indenide in the unobserved zwitterion **108**. These reactivity studies highlight the divergent stoichiometric substrate activation pathways that can be accessed by use of structurally analogous cationic and zwitterionic PGM species supported by donor-substituted indene and indenide ligands, respectively. Furthermore, the unusual reactivity of **108** with CH_3CN or Ph_2SiH_2 can be viewed as resulting from the cooperative action of the Lewis



Scheme 28. Neutral (**101**), cationic (**104**), and zwitterionic (**102**, **103**, **105**) platinum complexes derived from a P,S-indene ligand.



Scheme 29. Divergent cooperative activation of Ph_2SiH_2 by cationic (**107**) and putative zwitterionic (**108**) Cp*Ir complexes.

acidic Cp*Ir and Lewis basic indenide fragments in this zwitterionic complex,[118] in keeping with the apparent transformation of the putative zwitterion **81** into **78** upon treatment with excess H_2 or *i*PrOH (Scheme 24). On the basis of these preliminary observations, indenide-ligated PGM zwitterions appear to offer intriguing possibilities for the development of stoichiometric and catalytic substrate activation chemistry that is enabled by metal–ligand cooperative behavior.[119]

Although several isolated reports documenting the synthesis and characterization of alternative classes of zwitterionic PGM complexes of donor-substituted (hetero)carboranes (including **112**–**117**),[34,120–123] η^6-benzoates (including **118**),[124] deprotonated bis(phosphino)methanes (including **119** and **120**),[125,126] and an anionic N-heterocyclic carbene (**121**)[127] have appeared in the literature, the stoichiometric and catalytic reactivity of such species remains essentially unexplored. Selected structures are shown in Figure 5.

4. Sulfonate, Sulfate, and Phosphate-Based Ancillary Ligation

The synthesis, characterization, and catalytic application of the zwitterionic rhodium complexes **122** and **123**, which feature the anionic sulphos ligand, were first reported by Bianchini and co-workers in 1995 (Scheme 30).[128] The subsequent crystallographic characterization of **124**,[129] **125**,[130] and the iridium analogue of **122**[131] suggests that in this class of zwitterions, the sulfonate anion is spatially separated from the formally cationic PGM fragment. Although sulfonated phosphine ligands for use in preparing water-soluble transition metal complexes with applications in aqueous biphasic catalysis had been described previously,[132] the unique solubility profile of these zwitterionic sulphos complexes provided an entry point for the development of non-aqueous (alcohol/hydrocarbon) biphasic methods; **122** and **123** are not soluble in pure water, hydrocarbons, or diethyl ether, but do dissolve in light alcohols, such as methanol or ethanol, or in 1:1 (v/v) alcohol–water mixtures. Whilst an alcohol phase containing **122** or **123** separates from a hydrocarbon phase at ambient temperature, a single phase is formed reversibly above 60 °C. As such, homogeneous catalysis can be conducted above 60 °C, with catalyst recovery occurring under biphasic conditions at ambient temperature. A reactivity study revealed the utility of **122** and **123** as pre-catalysts for the hydrogenation and hydroformylation of alkenes under such biphasic conditions. For example, the hydroformylation of 1-hexene employing **123** as a pre-catalyst in methanol/isooctane afforded primarily alcohols under conditions whereby the related cationic catalyst system

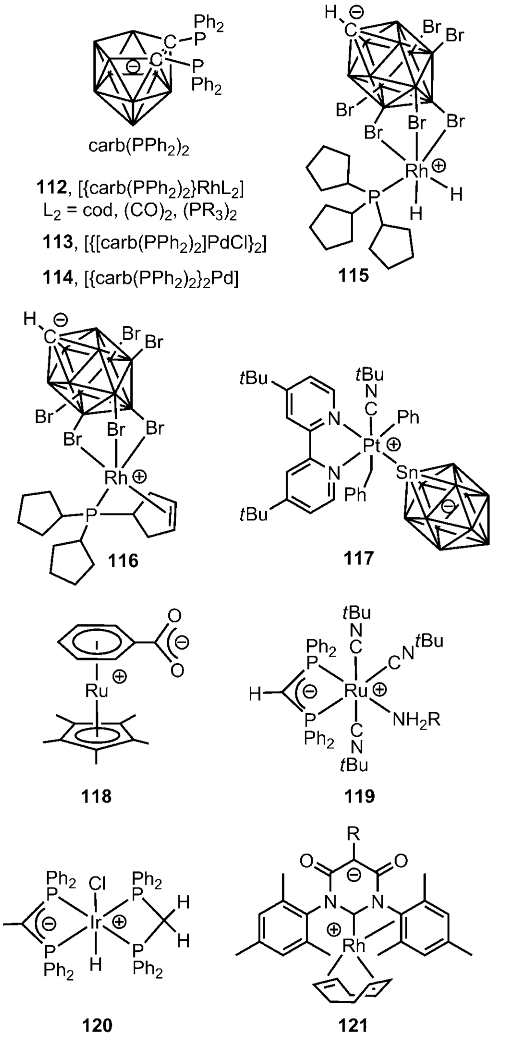
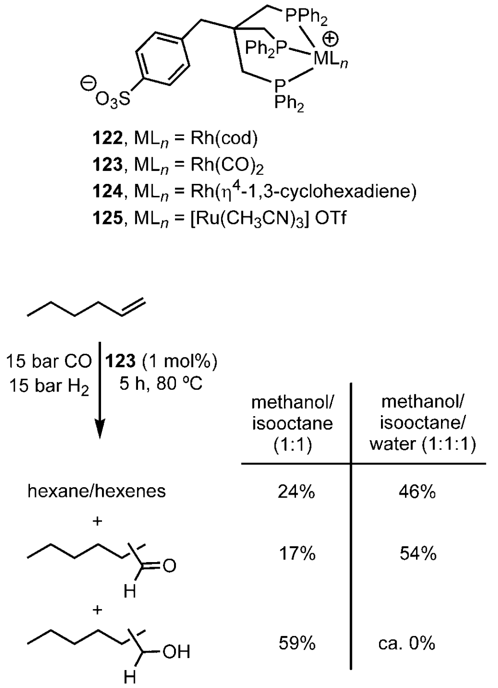
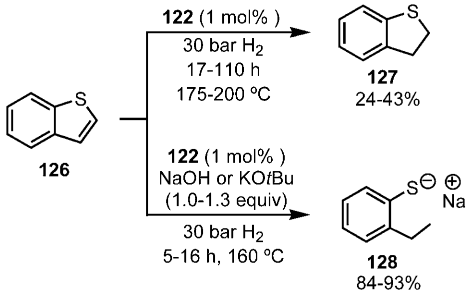


Figure 5. Alternative classes of zwitterionic PGM complexes featuring carbanions and related anions.



Scheme 30. Zwitterionic PGM sulphos complexes with applications in the hydroformylation of 1-hexene.

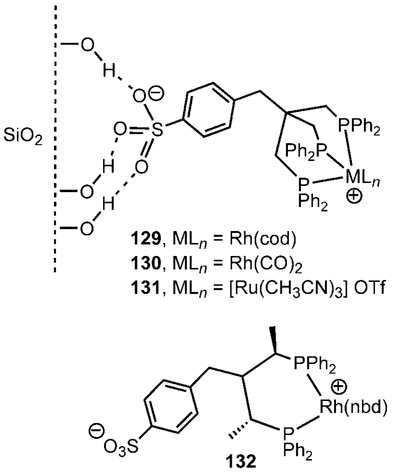


Scheme 31. Hydrogenation/hydrogenolysis of benzo[*b*]thiophene (**126**) mediated by the rhodium zwitterion **122**.

$[(\text{triphos})\text{Rh}(\text{dmad})]^+\text{BPh}_4^-$ (triphos = κ^3-$\text{CH}_3\text{C}(\text{CH}_2P\text{Ph}_2)_3$; dmad = dimethylacetylene dicarboxylate) produced aldehydes preferentially (Scheme 30).[128,131] The selective production of aldehydes can be achieved by using **123** in a mixture of methanol/isooctane/water, although under these conditions the overall conversion is lower.

The successful use of zwitterionic compound **122** as a precatalyst for the hydrogenation/hydrogenolysis of benzo[*b*]thiophene (**126**) in methanol, or under biphasic conditions comprising methanol or methanol–water as the polar phase and *n*-heptane as the organic phase, has been reported (Scheme 31).[133] Catalytic activity and selectivity was shown to not depend significantly on the phase variation. Whilst slow but selective conversion into the hydrogenation product **127** was observed under neutral conditions, in the presence of NaOH or other strong bases, fast and selective hydrogenolysis to **128** occurred (Scheme 31).

The capability of the sulfonate tail of sulphos to engage in hydrogen bonding has been exploited as a means of immobilizing PGM zwitterions on high-surface-area silica (Figure 6).[129–131,134,135] The grafted rhodium zwitterion **129** (i.e., **122**/SiO_2) was found to be an active catalyst for alkene hydrogenation under either solid–gas heterogeneous conditions using flow reactors for ethylene and propene, or solid–liquid heterogeneous conditions using batch reactors for styrene. The hydroformylation of 1-hexene employing **129** also occurred under solid–liquid heterogeneous conditions. However, under solid–gas conditions, **129** was transformed by CO/H_2 mixtures into the catalytically inactive dicarbonyl species **130**. Compared with the performance of **122** or **123** in hydrogenation and hydroformylation under liquid-biphasic conditions, the immobilized analogue **129** proved to be more chemoselective and recyclable than these unsupported zwitterions.[131] For example, when **129** was suspended in a hydrocarbon solvent for the hydroformylation of 1-hexene (Scheme 30), the conversion into aldehydes (88 %) exceeded the 54 % conversion attained when using **122** or **123** in methanol/isooctane/water; no rhodium leaching from **129** was observed. A hybrid catalyst comprised of **129** and palladium



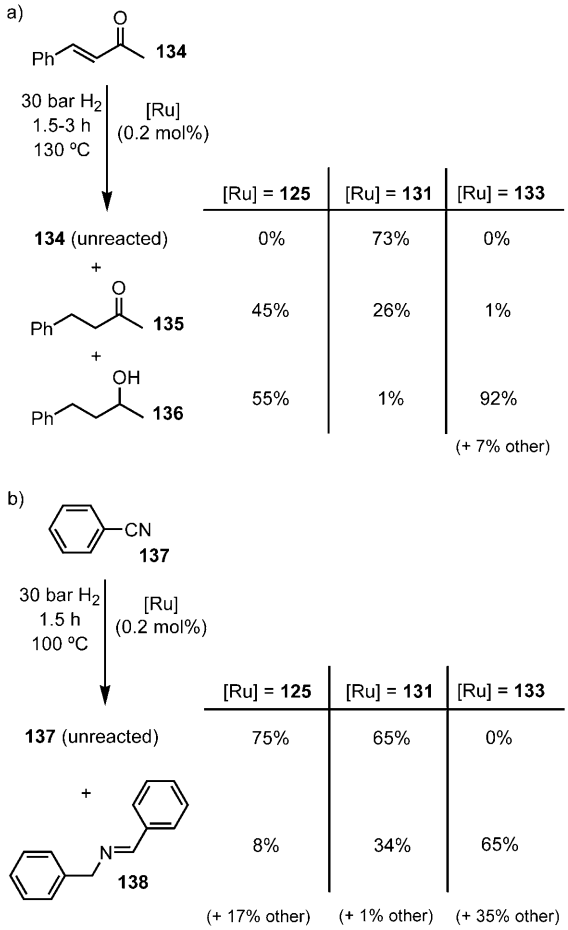
129, ML_n = Rh(cod)
130, ML_n = $Rh(CO)_2$
131, ML_n = $[Ru(CH_3CN)_3]$ OTf
132

Figure 6. Chiral and silica-supported PGM zwitterions featuring sulphos-type ligation.

nanoparticles has been shown to perform effectively for the hydrogenation of arenes.[129,135]

Although the efficacy of the chiral rhodium zwitterion **132** (Figure 6) in mediating the hydrogenation of prochiral alkenes has been demonstrated under homogeneous conditions, and under heterogeneous conditions using a silica-supported variant (i.e. **132**/SiO_2), only modest enantioselectivities (4–57 % *ee*) were achieved. Nonetheless, neither rhodium leaching (< 1 ppm) nor diminished catalytic activity was observed over the course of three consecutive heterogeneous runs using *n*-heptane as the reaction medium, which confirms further the efficacy of this catalyst immobilization strategy.[134]

A comparative study documenting the performance of the ruthenium zwittercation **125** (Scheme 30), the related silica-supported complex **131** (Figure 6), and the dicationic complex $[(triphos)Ru(CH_3CN)_3]^{2+}(OTf^-)_2$ (**133**) as pre-catalysts for the hydrogenation of unsaturated substrates has been published (Scheme 32).[130] Whilst **125**, operating under aqueous biphasic conditions (water/*n*-octane), afforded higher conversions than were achieved with the supported catalyst **131** (suspended in *n*-octane) for the reduction of benzylideneacetone **134**, this immobilized zwittercation catalyst exhibited high selectivity for the ketone product **135** over the alcohol **136**. Contrary selectivity was achieved by use of the dicationic pre-catalyst **133** in THF, whereby rapid consumption of **134** was observed, resulting in the preferential formation of **136**. In surveying the hydrogenation of benzonitrile **137** under similar conditions, the dicationic complex **133** proved to be more reactive than either of the zwitterions **125** or **131**; when using **133**, the consumption of **137** afforded a product mixture that included the imine **138** (65 %) and benzylamine (34 %). The supported species **131** out-performed the zwittercation **125**, affording almost exclusively **138**. For all of these reactions employing **125** or **131**, no appreciable ruthenium leaching was observed.[130]



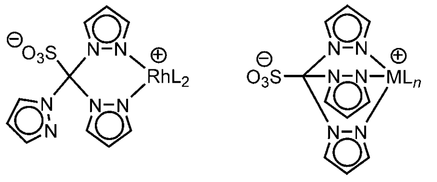
a)

	[Ru] = 125	[Ru] = 131	[Ru] = 133
134 (unreacted)	0%	73%	0%
+ **135**	45%	26%	1%
+ **136**	55%	1%	92%
			(+ 7% other)

b)

	[Ru] = 125	[Ru] = 131	[Ru] = 133
137 (unreacted)	75%	65%	0%
+ **138**	8%	34%	65%
	(+ 17% other)	(+ 1% other)	(+ 35% other)

Scheme 32. Reduction of a) benzylideneacetone (**134**) and b) benzonitrile (**137**) mediated by the ruthenium zwittercation **125**, the related silica-supported complex **131**, and the dicationic ruthenium complex **133**.

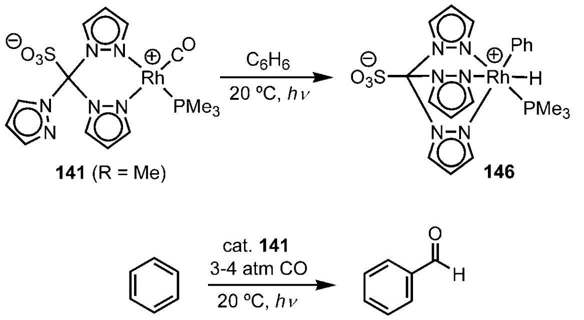


139, L_2 = cod
140, L_2 = $(CO)_2$
141, L_2 = (CO, PR_3)
142, ML_n = Rh(nbd)
143, ML_n = $Ir(C_2H_4)_2$
144, ML_n = $Ir(C_2H_4)(PR_3)$
145, ML_n = $Ir(H)_2(PPh_3)$

Figure 7. Zwitterionic Group 9 complexes featuring tpms ligands.

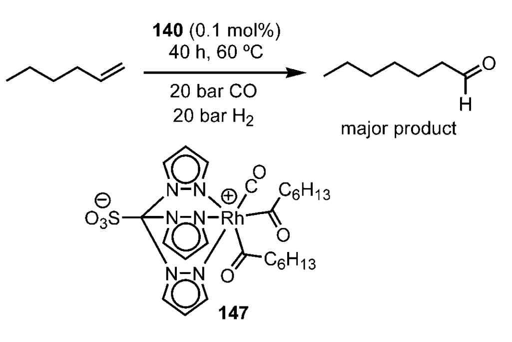
The synthesis and reactivity of rhodium and iridium coordination complexes of tris(pyrazolyl)methanesulfonate (tpms) have also appeared (Figure 7). Unlike more common $\kappa^{2/3}$-tris(pyrazolyl)borate (Tp) PGM species, for which resonance delocalization of the borate anionic charge onto the nitrogen donors leading to non-zwitterionic complexes is prevalent, analogous complexes of tpms that feature only M–N linkages can be viewed as being formally zwitterionic. The capacity of tpms to support square planar (**139**–**141**), five-coordinate (**142**–**144**), and six-coordinate (**145**) PGM complexes in a manner similar to Tp has been confirmed by methods that include crystallographic techniques.[116,136,137] Whilst in the crystal structure of the κ^2-*N,N* zwitterion **140** the pendant sulfonato fragment was observed to be proximal to the rhodium center, the shortest Rh···O distance (2.8941(18) Å) exceeds the sum of the van der Waals radii for these elements.[136] However, subsequent reports documenting the ability of tpms and related ligands to form non-zwitterionic κ^3-*N,N,O* complexes featuring a M–O–SO_2R linkage (M = Co, Cu, and Zn) suggest that this class of ancillary ligands is not generally effective in rigorously enforcing a zwitterionic structural motif.[138–143]

Irradiation of **141** (R = Me) in benzene afforded **146**, the isolable product of hydrocarbon C–H oxidative addition (Scheme 33). The zwitterionic compound **141** was also shown to be a competent pre-catalyst for the formation of benzaldehyde by carbonylation of benzene, and it is able to achieve 20 turnovers over the course of 24 h.[144]

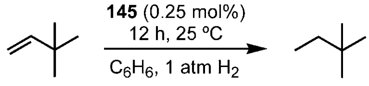


Scheme 33. C–H bond activation and carbonylation of benzene mediated by the rhodium zwitterion **141**.

The application of the zwitterion **140** (or alternatively **139** as a source of **140**) as a pre-catalyst for the hydroformylation of 1-hexene has also been examined.[145] Acetone proved to be superior to toluene, THF, and acetonitrile for this reaction, and in all cases the linear hydroformylation product *n*-heptanal was generated as the major product (Scheme 34); the linear regiochemistry attained from **140** contrasts that obtained by use of related TpRh derivatives. Spectroscopic analysis of the catalytic reaction mixtures revealed the formation of the isolable zwitterionic bis(acyl) complex **147**, which was found to possess the same catalytic activity of **140**.[145] More recently, the zwitterionic iridium complex **145** was shown to catalyze the hydrogenation of 3,3-dimethyl-1-butene to 2,2-dimethylbutane under relatively mild conditions (Scheme 35).[116]

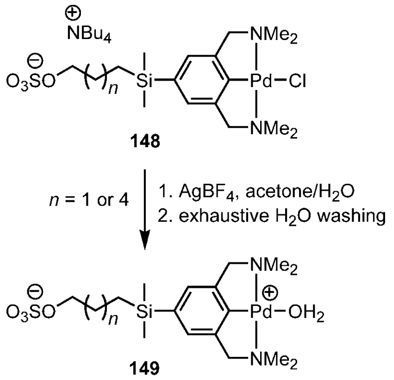


Scheme 34. Hydroformylation of 1-hexene employing the rhodium zwitterion **140** as a pre-catalyst.



Scheme 35. Hydrogenation of 3,3-dimethyl-1-butene employing the iridium zwitterion **145** as a pre-catalyst.

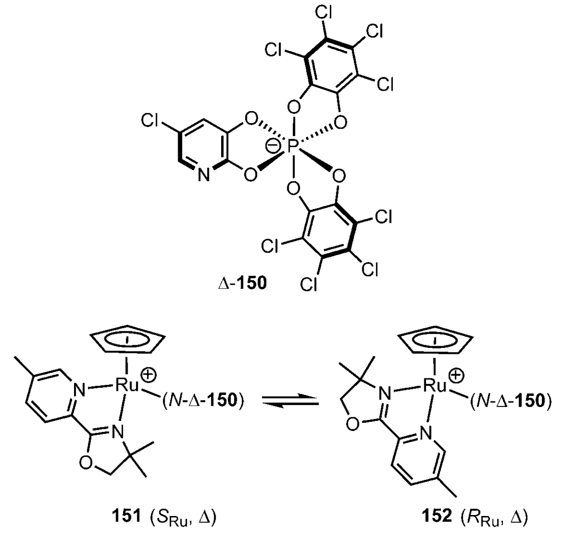
Zwitterionic arylpalladium pincer complexes featuring tethered sulfato fragments have been reported (Scheme 36).[146] Exposure of the ammonium salts **148** to halide abstraction conditions in the presence of water afforded the corresponding zwitterionic palladium aqua complex **149**. Despite the hydroscopic nature of **149**, these complexes are soluble in a range of organic solvents, but are insoluble in water. On the basis of IR data, **149** is proposed to adopt a dimeric structure in which a weakly coordinated sulfato group of an adjacent molecule of **149** is hydrogen-bonded to the coordinated aqua ligands.[146] In this vein, the hydrogen-bonding capability of the sulfato tail in **148** and **149** has been exploited in the preparation of metallodendritic assemblies.[147]



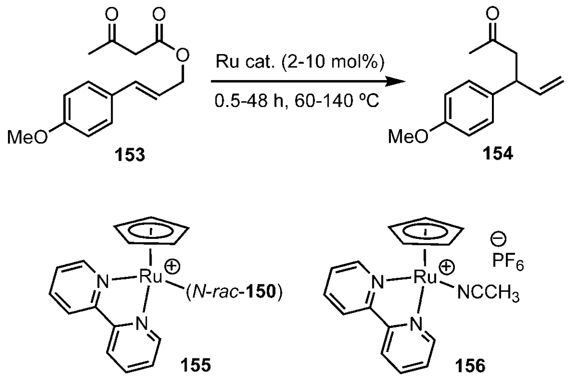
Scheme 36. Preparation of the zwitterionic palladium pincer complex **149**.

The introduction of a peripheral pyridyl fragment into the skeleton of enantiopure tris(tetrachlorobenzenediolato)phosphate provides access to a distinct class of chiral zwitterionic metal complexes (Scheme 37).[148,149] Coordination of resolved **Δ-150** to CpRu species bearing N,N-coligands allows for stereocontrol of the ruthenium center. For the system **151/152**, a diastereomeric ratio (d.r.) of 72:27 was observed in CD_2Cl_2, whereas in CD_3NO_2 the ratio was 80:20; d.r. values of up to 96:4 were obtained by altering the nature of the N,N-ligand. The anion **Δ-150** also performed effectively as a chiral auxiliary in controlling the conformation of *tropos* coligands within the coordination sphere of CpRu zwitterions with high selectivity.[148]

A comparative study examining the regioselective Carroll rearrangement of **153** into **154** mediated by the zwitterion **155** or the related cationic complex **156** revealed several reactivity benefits associated with the use of the zwitterionic pre-catalyst in this transformation (Scheme 38).[149] Whilst both **155** and **156** afforded **154** cleanly in reactions conducted in THF at 60 °C (10 mol% Ru), **156** required only 4 h reaction time, whereas 48 h were required when using the zwitterionic



Scheme 37. Interconversion of the zwitterionic ruthenium diastereomers **151** and **152**, which feature the enantiopure ligand **Δ-150**.



Scheme 38. Regioselective Carroll rearrangement of **153** into **154** catalyzed by the ruthenium zwitterion **155** or the related cationic complex **156**.

pre-catalyst **155**. However, unlike cationic species **156**, the lipophilic character of **155** enabled the efficient recovery of this zwitterion from the crude reaction mixture by use of column chromatography; five subsequent re-use cycles were conducted without loss of efficiency or regioselectivity. Raising the reaction temperature to 140 °C by use of microwave irradiation resulted in an erosion of regioselectivity when using **156**; however, clean conversion into **154** was achieved by use of zwitterionic **155** under similar conditions. Furthermore, asymmetric variants of this rearrangement employing dinuclear relatives of **155** and **156** (THF, 60 °C) supported by chiral tetradentate nitrogen ligands proceeded with higher enantioselectivity (in **154**) when using the dinuclear zwitterionic pre-catalyst (85 % *ee*) in place of the analogous cationic the pre-catalyst (57 % *ee*).

5. Summary and Outlook

Advances in ancillary ligand design have enabled the development of several distinct classes of zwitterionic PGM complexes that feature enforced formal charge separation between a cationic metal fragment and an anionic moiety sequestered within a coordinated ancillary ligand. Such zwitterions are capable of mediating a range of stoichiometric and catalytic σ-bond activation processes. Although the breadth of comparative reactivity studies of structurally related cationic and zwitterionic PGM species is still somewhat limited, the reports published to date reveal that depending on the system under investigation, the reactivity of such zwitterions can be analogous to or divergent from that of more conventional cationic PGM species. In this regard, when issues of catalytic activity/selectivity and solvent compatibility are considered, PGM zwitterions have emerged as complementary alternatives to more conventional neutral and cationic complexes. In several of the zwitterionic systems examined herein, participation of the sequestered anionic moiety within the ancillary ligand during the course of reactivity sequences has been documented. If properly exploited, such ancillary ligand non-innocence[119] may provide inroads to useful new modes of cooperative metal–ligand bifunctional substrate activation. Future advances in the design of zwitterionic PGM species will benefit tremendously from experimental/computational analyses of charge density as a means of better understanding the electronic structure of conventional cationic PGM species, as well as to quantify the extent to which charge separation exists within a given zwitterionic framework. We anticipate that such investigations will give rise to entirely new classes of zwitterionic PGM complexes that exhibit novel reactivity patterns.

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[8] For the purposes of the discussions herein, zwitterionic complexes are defined as those species that formally lack conventional Lewis resonance structures that place an anionic charge onto one of the donor atoms of the ancillary ligand. Under this formalism, coordination complexes of many common ligands, including (pyrazolyl)borates, acetylacetonates, and β-diketiminates, for which resonance delocalization of the anionic charge onto the donor atoms is likely to be prevalent, are not classified as zwitterionic. Dinuclear complexes that feature formally cationic and anionic PGM centers fall outside the scope of this review.
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