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SCORPIONATES: PINCH AND STING... THE METAL

Poly(pyrazolyl)borates have proven to be extremely popular ligands since their introduction by Trofimenko. The basic skeleton of the ligand involves pyrazole units bonded to a boron apex via the nitrogen atoms at the displacement of hydrogen.
The manner in which they combine with metal ions reminded him of the grabbing-and-stinging action of a scorpion, hence he coined for them the term "scorpionates". An overview of progresses reached with scorpionate ligands, together their potentiality in materials science, catalysis, C-H bond activation and bioinorganic chemistry is given.

Since their discovery in the mid 1960 (1-6), poly(pyrazolyl)borates (Figure 1), often indicated as scorpionates, have been considered as some of the most useful ligand in modern coordination chemistry. Their versatility derives from the different steric and electronic effects that can be attained by varying the nature, number and position of the substituents in the pyrazole rings in order to fine-tune the reactivity at the metal centers.

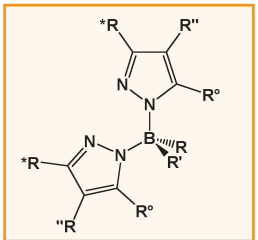


Figure 1 - General structure for a poly(pyrazolyl)borate ligand: R = or π R' ≠ H, alkyl, aryl, halide or pyrazole; R*, R°, R" = H, alkyl, aryl, halide or ester

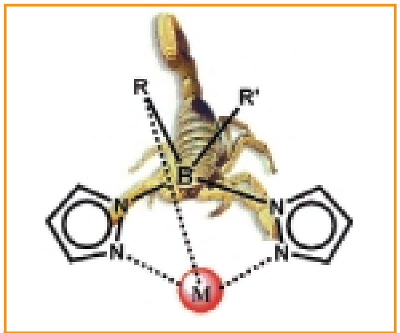
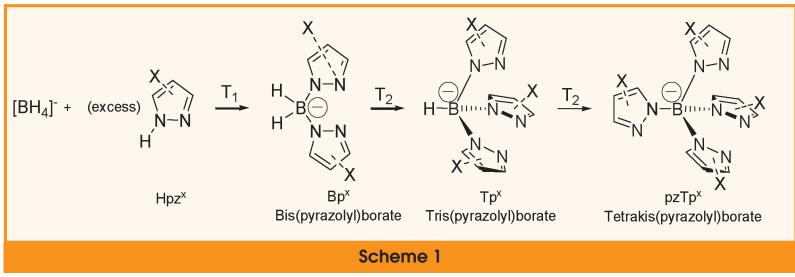


Figure 2 - The scorpion uses its claw like pincers to grab its prey

The term scorpionate has been used to describe the interchange between bidentate and tridentate coordination modes of these ligands.

Like the pincers of a scorpion (Figure 2), these versatile tripodal ligands introduced by Trofimenko (Figure 3) bind a metal with nitrogen heteroatoms from two pyrazole rings attached to a central boron atom. The third pyrazole ring (or the R group), attached to the boron, rotates forwards like a scorpion's tail to "sting" the metal. These ligands have been employed for the synthesis of complexes with virtually every metal in the periodic table, having application from homogeneous catalysis to bioinorganic chemistry.



Scheme 1

Figure 3 - Trofimenko between A. Cingolani (right) and C. Pettinari (left) at 225th ACS Meeting (New Orleans, 2003)

The most commonly used members of this class are the tris(pyrazolyl)borate ligands (generally abbreviated as Tp^x) which are formally analogous to cyclopentadienyl (Cp) ligands in that both are six-electron (ionic model) or five-electron donor (covalent model) ligands. They are weak-field hard σ-N donors which tend to form *fac*-octahedral complexes, while Cp ligands are typically 5-fold π-donors and tend to form tetrahedral complexes. Comparatively, their overall donor properties are weaker than those of the cyclopentadienyls. They are bulkier than the cyclopentadienyls and moreover in six-coordinate environments they enforce nearly octahedral coordination to the metal with N-M-N bite angles close to the ideal 90° value. The Tp^x ligands are able to grab the top half of a metal so that it is possible to mess around with the other half. They may act as more than simple spectators in the course of chemical reactions experienced by their compounds, and have an important influence on their reactivity by means of temporary changes of denticity.

The fundamental feature in all poly(pyrazolyl)borate complexes is the six-membered ring within a more general structure $RR'B(\mu\text{-}pz)_2M(L)_n$ (Figure 4).

Synthesis of poly(pyrazolyl)borate ligands can be efficiently performed by heating tetrahydroborate ion in molten pyrazole (Scheme 1).

Two different class of scorpionate ligands may be distinguished. The first is homoscorpionates, where the pseudoaxial R group is another pyrazolyl group (pz^x) identical to the two bridging pz^x groups. In this case the ligand is tridentate and has a local C_{3v} symmetry. The unsubstituted tris(pyrazolyl)borate (Tp) and its 3,5-dimethyl analog (Tp*) are the most commonly employed members of this class. The second is *heteroscorpionates*, where the coordinating pseudoaxial R group is anything but pz^x. Heteroscorpionates also include ligands where R is another pyrazolyl group (pz^y) different from pz^x. Tris(pyrazolyl)borates, Tp^x, generally coordinate as tridentate ligands through three nitrogen atoms of the pyrazole rings κ^3-N,N',N'' (Figure 5a), thereby providing effective steric shielding of the metal center (1-6, 7)

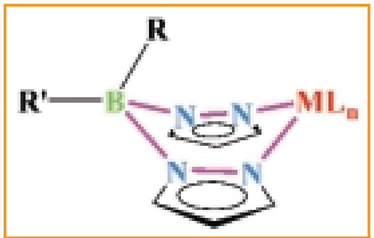


Figure 4 - The six membered ring B-N-N-M-N-N-B

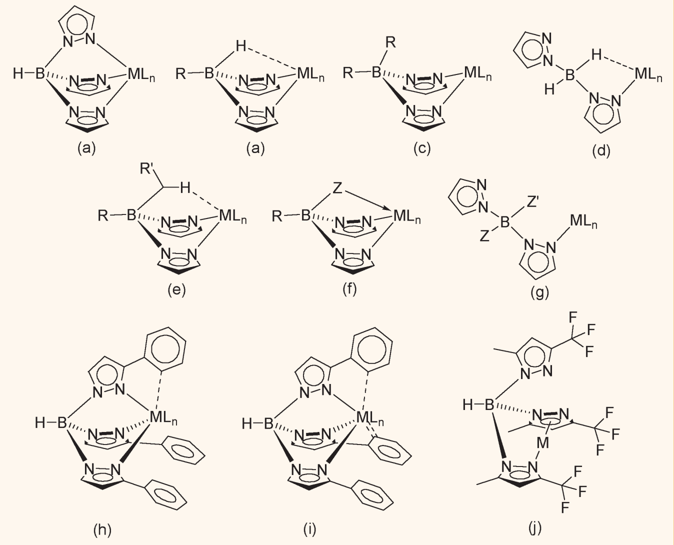


Figure 5 - Selected coordination modes for scorpionate ligands

By introducing suitable substituents (e.g. Me, CF_3, *t*Bu, Ph) in the 3-position of the pyrazolyl rings this effect can be tuned to a large extent: the tridentate κ^3-*N,N',B-H* type (Figure 5b) (8), the bidentate κ^2-*N,N'* (Figure 5c) (9) and κ^2-*N,B-H* coordination (Figure 5d) (10) are then possible. Formation of agostic B-H-M bonds is relatively easy with Bp^x ligands, whereas the agostic B-C-H-M (Figure 5e) bond does not occur very frequently. $R(Z)Bp^x$ are generally tridentate, due to the presence of a heteroatom Z which can coordinate to the metal (Figure 5f). Lower denticity, such as κ^1-*N*, has been also reported in selected cases (Figure 5g) (11, 12). Tetradenticity has been reported in Tp^x either by way of agostic bonding, or through cyclometalation taking place at one of the aliphatic R groups per ligand (Figure 5h) (13). An unusual κ^5 coordination of hydrotris(3-phenylpyrazolyl)borate ligands (Tp^{Ph}) has been recently reported (Figure 5i) (14). Despite the formal similarities with the Cp a π interaction between a pyrazolylborate ligand and a metal center (Figure 5j) has been recently found only in $\{[(KTp^x)_2(CuCO_3)]_2\}$ (15).

Complexes with all metal and metalloids of the periodic Table have been synthesised. Trofimenko reported in 1986 (16) and in 1993 (17) two reviews on the coordination chemistry of poly(pyrazolyl)borates whereas in a book published on 1999 (18) the king of

Selected major reference works concerning scorpionate chemistry

Main Author	Topic	Ref
Canty	Pd and Pt derivatives of Tp^x	(26)
Dias	Fluorinated Tp^x ligands and their interaction with metals	(27)
Enemark	Mo(Tp^x) containing enzymes models	(28)
Etienne	Tpx derivatives of V, Nb and Ta	(29)
Janiak	Tl derivative of Tp^x	(30)
Kirchner	Ruthenium Tp^x chemistry	(31)
Kitajima, Tolman	Organometallic and bioinorganic chemistry of hindered Tp^x ligands	(32)
Kitajima, Moro-Oka	Copper-dioxygen complexes of Tp^x	(33)
McCleverty	Mo and W derivatives of Tp*	(34)
McCleverty; Ward	Supramolecular chemistry of Tp^{Py}-based ligand	(35)
McCleverty; Ward	Bridged polynuclear complexes of Mo with scorpionate ligands	(36)
Niedenzu	Pyrazaboles	(37)
Parkin	Metal hydroxides, hydrides and organometallics of hindered Tp^x	(38)
Parkin	Grignard reagents	(39)
Parkin	Carbonic anhydrase models	(40)
Pettinari; Santini	A survey of poly(pyrazolyl)borates and related ligands and their coordination compounds from 1980 to 2003	(41)
Pettinari	A survey of tris(pyrazolyl)methanes and related ligands	(42)
Pettinari	A survey of bis(pyrazolyl)methanes and related ligands	(43)
Shaver	A survey of poly(pyrazolyl)borate and related ligands and their coordination compounds until to 1980	(44)
Reger	Ga and In derivatives of poly(pyrazolyl)borates	(45)
Santos and Marques	Tris(pyrazolyl)borate ligands in lanthanides and actinides complexes	(46)
Slugovc and Carmona	C-H activation and coordination chemistry of rhodium- and iridium-trispyrazolylborate complexes	(47)
Theopold	Dioxygen activation with Tp^x-Co complexes	(48)
Vahrenkamp	Zinc pyrazolylborate chemistry related to zinc enzymes	(49)
Young and Wedd	Mo and W-pterin analogues	(50)
Several authors	Scorpionates symposium at ACS 2003	(51)

scorpions has summarized all results reported in literature with these ligands (>2,000 references). All of the Tp ligands have a cone angle (θ) larger then 180°. The ligands of small cone angle are characterized by a strong tendency to form $Tp^x{}_2M$ complexes with divalent first row transition metals, and the inability to form stable Tp^xMR species. When R is a small molecule or anion the half-sandwich mononuclear species Tp^xMR can be considered as the model complexes of metalloenzymes.

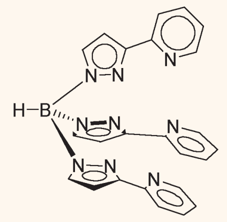


Figure 6 - Structure of the Tp^{py} ligand

Scorpionate ligands have been employed in high-valent Mo and W chemistry related to various enzymes (19) and also in the stabilization of low-valent Mo and W (20). Parkin used the second generation poly(pyrazolyl)borates (21, 22), having bulky substituents such as *t*-Bu or Ph in the 3-position, developed after 1986, to stabilize monomeric alkylmagnesium, alkylzinc and alkylberillium species (23). Mayer reported the use of the Tp^x ligands to stabilize strongly oxidizing osmium oxo and nitride complexes (24). The versatility of the pyrazolylborate ligands system can be seen in the Tp^{py} (Figure 6) coordination chemistry. Tp^{py} derivatives, as for example $[U(Tp^{py})_2]I$ in which 12 nitrogen atoms are coordinated to a single uranium atom, exhibit remarkable structural features (25). The ligand Tp^{py} permits also encapsulation of lanthanide metals which have a much higher coordination number.

A number of reviews and papers were devoted to scorpionates and related systems, selected relevant subjects being reported in the Table above.

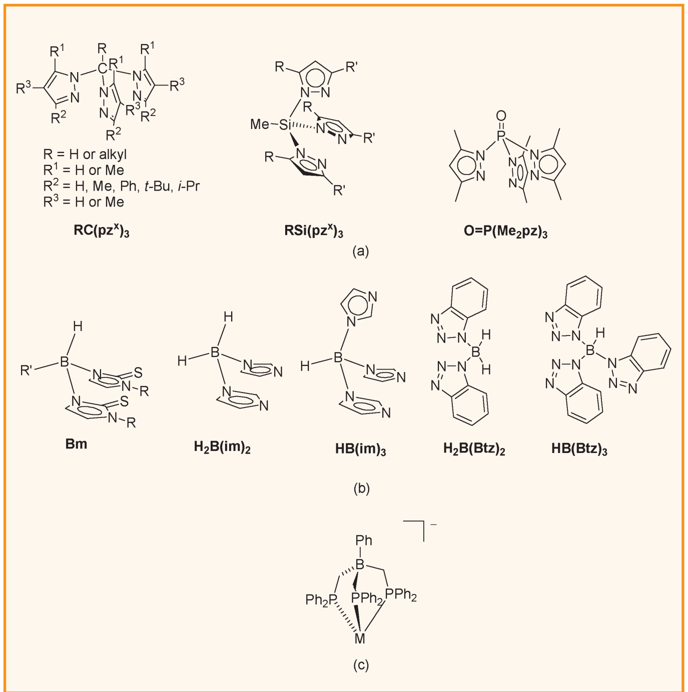
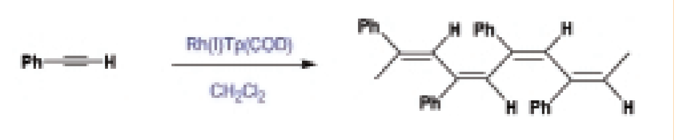


Figure7 - Not-classical scorpionates: (a) ligands containing different bridging atoms; (b) ligands containing different heterocyclic rings; (c) phosphinomethylborate ligands leading to zwitterionic complexes

As shown in Figure 7a the bridging boron atom of a poly(pyrazolyl)borate can be replaced by a carbon, silicon, phosphorus or gallium atom. Several researchers have often contrasted the chemistry of complexes of the neutral isosteric and isoelectronic poly(pyrazolyl)alkanes with that previously developed for anionic poly(pyrazolyl)borates, so that a number of differently-charged complexes with structures analogous to those reported for Tpx derivatives have been obtained. Tris(pyrazolyl)alkanes in particular are suitable for the stabilization of air-unstable group IA compounds and for the synthesis of supramolecular silver and copper complexes (52).

For a long time only a few poly(azolyl)borate complexes with azolyl groups other than pyrazole have been investigated (Figure 7b), although it has been shown that the chemistry of poly(azolyl)borate complexes may be critically dependent on the pattern of ring substitution (53). This aspect has induced several researchers to study the behavior of metal complexes of analogous ligand systems with modified steric and/or electronic properties, such as poly(tetrazolyl)borate (54), poly(1,2,3-benzotriazolyl)borate (55), poly(2-sulfanyl-1-methylimidazolyl)borate (56) and poly(imidazolyl)-borate ligands (57). These modifications however have lead to new scorpionates capable of bridging different metal centers, yielding dimers or coordination polymers characterized by peculiar spectroscopic and structural features.



Scheme 2

Some of these new ligands are very promising for the synthesis of inorganic materials with inner cavities useful for the catalysis of organic reactions (58) or with collective magnetic phenomena for the design of molecular-based ferromagnets (59). Two never types of boron-based ligands recently described are the phosphinomethylborates (60) ($((PhB(CH_2PR_2)_3)^-$, Ph = phenyl, R = aryl or alkyl) (Figure 7c) and the aminomethylborates ($((Ph_2B(CH_2NMe_2)_2)^-$, Me = methyl) (61). The phosphinomethylborate ligands are hybrids inspired in part by Trofimenko's pyrazolylborates, but also by the useful donor features of simple tertiary phosphine ligands, whereas the aminomethylborate ligands are reminiscent of tertiary diamines. The phosphorus or nitrogen donor arms serve to partially insulate the negative charge of the borate unit from the metal ion, leading to complexes that are formally zwitterionic.

New materials

Ligands as those in Figure 8 can be employed as building blocks for the generation of oligonuclear aggregates and metal-containing polymers. It has been reported that bulky substituents attached to the boron centre seem disfavour an η^3-binding mode of the scorpionate ligand likely due to steric congestion (62). As a consequence, oligomeric structures may be established in complexes with weak metal nitrogen bonds (62).

The charge-neutral ligands poly(pyrazolyl)methanes isosteric and isoelectronic with pyrazolylborates and their isotopic derivatives have been employed to build highly symmetrical supramolecular silver, manganese and iron complexes. The physical and photophysics properties of the new systems are being explored for possible application as sensors and catalysts (63).

An interesting example of materials application has been recently reported by Boncella's group: electroluminescent lan-

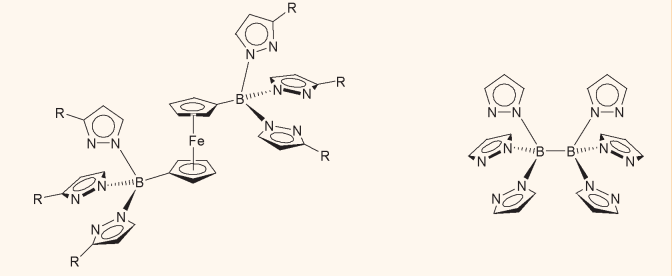


Figure 8 - Multitopic scorpionate ligands able to form coordination polymers

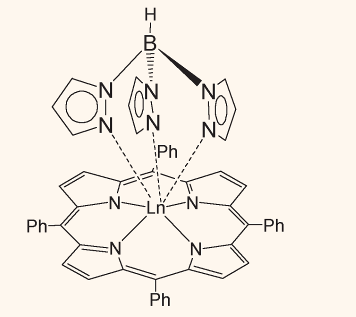


Figure 9 - An electroluminescent lantanide complex containing a Tp ligand coordinated in tripodal fashion

thanide complexes containing Tp^x ligands (Figure 9) have been incorporated in the active layer of polymer light-emitting diodes (PLEDs). The Tp^x ligand binds the top half of the lanthanide metal and a tetraphenylporphyrin ligand binds the lower half, encapsulating the lanthanide ion and shielding it from outside interactions (64). This kind of compounds have enhanced luminescence efficiencies compared with analogous containing mono or bidentate ligands.

Catalysis

Tris(pyrazolyl)borates are also widely used in the developments of catalysts, mainly for polefin polymerization. Yttrium complexes of Tp^x can catalyze the polymerisation of ethylene to give linear polyethylene (65). One advantage of this catalyst system over metallocene based catalytic system is the ease of modify the Tp^x ligand to change the steric and electronic properties of the complex. Theopold and coworkers used some $Tp^xCr(II)$ alkyl complexes as mononuclear, homogeneous models of the Union Carbide catalyst, in order to better understand the structure and the mechanism of the catalytic species (66). Several studies have indicated that $Tp^xTiCl_n(OR)_{3-n}$/MAO catalysts (n= 1-3) (where the scorpionate is not sterically hindered) polymerize ethylene, ethylene/α-olefins, and styrene, the activity of the catalyst being however poor and the polymers having a broad molecular weight distributions (67). On the other hand Tp^xTiCl_3 and Tp^xTiCl_2OR (where Tp^x is a sterically hindered ligands containing for example mesityl groups on the 3-position of the heterocyclic rings) exhibit high activity and produce linear polyethylene. The predominant chain transfer mechanism in ethylene polymerization by Tp^xTiCl_3/MAO is chain transfer to MAO and the $AlMe_3$ contained therein (68). The polymerization of ethylene has been investigated using niobium, yttrium, vanadium, titanium and nickel-Tp^x complexes.

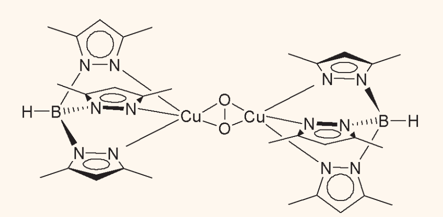


Figure 10 - Structure of the dinuclear $(Tp^*Cu)_2(\mu\text{-}O)_2$

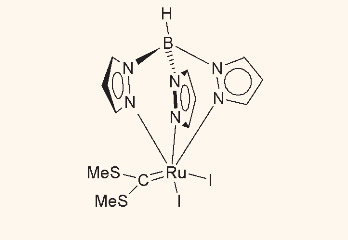


Figure 11 - A carbene complex containing a scorpionate ligand

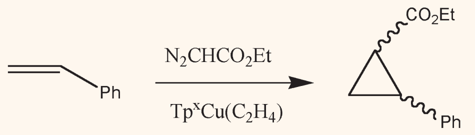
$Tp^xRh(COD)$ derivatives (Tp^x = sterically hindered homoscorpionate and COD = 1,5-cyclooctadiene) have been employed in the homopolymerization of phenylacetylene derivatives containing different para-substituents (Scheme 2) (69). RhTp(COD) was also employed for the regioselective homogeneous hydrogenation of quinoline (70). $RhTp^*(C_2H_4)(PEt_3)$ catalyzes the dimerization of terminal alkynes (71). $RhTp^*(C_2H_4)_2$ is active for the catalytic hydrosylilation of ethylene.

Copper scorpionate derivatives such as Tp*Cu(ethylene) catalyze under mild condition the reaction of ethyldiazoacetate with alkenes to form cyclopropanes (Scheme 3) (72). Trofimenko's most recent work includes functionalization of aliphatic C-H bonds with a brominated scorpionate copper(I) catalyst, $Tp^{Br3}Cu(MeCN)$. The Tp^{Br3} ligand, having nine bromine atoms, three on each pyrazolyl ring, is the only one ligand devoid of C-H bonds. It has been reported that the $Tp^{Br3}Cu(MeCN)$ catalyst provide good yields and high selectivity and is in an improvement over other copper catalysts for inserting ethyl diazoacetate into tertiary C-H bonds of alkanes (73). The application of $RuTp^x$ complexes in catalytic transformation of organic molecules, such as the dimerization and polymerization of acetylenes and hydrogenation of ketones has been also described (31).

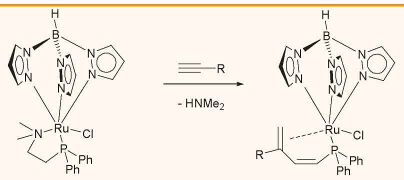
Scorpionati: "pizzicare" e "pungere" il metallo

ABSTRACT

I polipirazolilborati, introdotti da Trofimenko, sono oramai annoverati tra i più comuni leganti azotati. La loro versatilità deriva dalla natura, dalla posizione e dal numero dei sostituenti che possono essere collocati sull'anello pirazolico o sull'atomo di boro a ponte, così da consentire una modulazione "fine" della reattività e delle proprietà del centro metallico. Come le pinze di uno scorpione, questi versatili leganti tripodali legano il metallo con gli atomi di azoto degli anelli pirazolici. Nell'articolo vengono riassunti i principali risultati conseguiti con tali molecole, unitamente ad una descrizione delle loro potenzialità nella campo della chimica dei materiali, nella catalisi, nell'attivazione del legame C-H e nella chimica bioinorganica.



Scheme 3



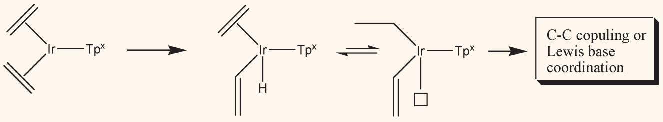
Scheme 4

Bioinorganic chemistry

Scorpionate ligands have been mainly employed as models for bioinorganic systems to help in efforts to understand the structure and function of the binding sites of metalloenzymes in which the metal is coordinated to two or three imidazolyl nitrogens from three hystidine ligands, such as haemocyanin, ascorbate oxidase, superoxide dismutase, hemerythrin and carbonic anhydrase. Kitajima and coworkers synthesised the μ-peroxo bridged $(Tp^*Cu)_2(\mu\text{-}O)_2$ (Figure 10) by hydrogen peroxide oxidation of $(Tp^*Cu)_2(\mu\text{-}O)$. The O-O IR stretching frequency in $(Tp^*Cu)_2(\mu\text{-}O)_2$ is very close to that found in oxyhaemocyanin (a protein transporting oxygen in arthopods and molluscs) (33).

The same authors have prepared some Tp^x Fe and Mn dioxygen complexes which serve as appropriate synthetic models for a variety of enzymes, including non-heme iron dioxygen carrier, non-heme iron oxygenases, and water oxygenation center in photosynthetic system II (74).

Methyl substituted tris(pyrazolyl)borates have been also used in the modelling of molybdenum enzymes containing a single metal atom and a 6-substituted pterin ring system (50). The Tp^x ligands act as facial blocking agents for three coordination sites and focuses the reactivity onto the three remaining sites, the presence of a methyl group in the 3-position of Tp^x inhibiting dinucleation. The major efforts in modelling zinc-based enzymes have been devoted to carbonic anhydrase models (75). Tp^x ligands sterically hindered have been developed and used on order to obtain $Tp^xZn(OH)$ without formation of sandwich Tp^x_2Zn systems. $Tp^xZn(OH)$ reacts generally rapidly and reversibly with carbon dioxide forming carbonate complex $Tp^xZn(OCO_2H)$. $Tp^xZn(OH)$ has been demonstrated to be a functional model of carbonic anhydrase. A series of $Tp^xFe(\mu\text{-}O)(\mu\text{-}OOCR)_2$ has been prepared with the aim to model hemerythrin whereas $Tp^xFe(OOCPh)(MeCN)$ has been described as a synthetic modes for dioxygen binding sites of non-heme iron proteins. Also some manganese complexes of formula $Tp^xMn(OBn)$ and $Tp^xMn(OBn)(Hpz)$ have been investigated as models of manganese superoxide dismutase (76).



Scheme 5

C-H activation

The synthesis of highly reactive vinylidene complexes and their involvement in stoichiometric C-C coupling reactions with activated alkanes and olefins has been summarized by Kirchner and coworkers (31). Neutral vinylidene complexes are key intermediates in alkyne insertion reactions into aliphatic C-H bonds. For example when the complex (Ru(Tp)Cl(P,N-donor)) (Scheme 4) reacts with terminal alkynes HC=C-R* yields a coupling product of the alkyne and of the P,N-donor ligand (77).

It has been reported that double aklkylation of the carbon disulfide adducts $(Rh(\eta^2\text{-}SCS)(Tp)(PPh_3))$ with iodomethane resulted in the carbene complex $(RhI_2(=C(SMe)_2)(Tp))$ (Figure 11) through loss of the remaining phosphine ligand (78).

The transformation of transition metal ethylene complexes into their hydride-vinyl isomers is typically thermodynamically uphill for mononuclear systems. The only exception to this rule, up to now, are the Ir(I) olefin Tp^x complexes. At variance with the analogous IrCp(III) system, $IrTp^x$ hydride-vinyl derivatives are found to be the product of the thermal or photochemical activation of the Ir(I) olefin species $IrTp(\eta^2\text{-}C_2H_4)L$. This unusual behaviour may be traced to the properties of the Tp^x ligand, first, its hard nature (as compared with the Cp), and its favourable binding interaction with the harder Ir(III) center; and second its well-known propensity to impose octahedral-coordination at the metal center which is highly favourable for d^6 Ir(III) (47).

For example $IrTp(C_2H_4)_2$ converts to $IrTp(C_2H_4)(H)C_2H_3$ upon irradiation (Scheme 5). This compound is thermodynamically favoured and may be trapped by a donor (MeCN, cyclic ethers) or undergo C-C coupling to finally give their hydride-allyl isomers (79).

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