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Ligand-Based Reactivity of a Platinum Bisdithiolene: Double Diene Addition Yields a New C_2-Chiral Chelate Ligand

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The reaction of $Pt(tfd)_2$ [tfd=$S_2C_2(CF_3)_2$] with excess 2,3-dimethyl-1,3-butadiene initially yields the expected 1:1 adduct, in which the diene has added across two sulfur atoms on separate tfd ligands. However, within 1 day at 50 °C, this kinetic product quantitatively converts into a thermodynamic product where two dienes have added to one tfd ligand via unprecedented addition across the dithiolene CS bonds. The new reaction is highly selective for the C_2-symmetric diastereomer. A new chiral bisthioether chelate ligand has formed in the product, which has been characterized crystallographically.

The study of reactions between alkenes and metal complexes has yielded both tremendous insight and a wealth of useful applications.[1] In many reactions, the alkene coordinates directly to the metal center, forming a metal−alkene complex.[2] Alkenes can also interact with metal complexes having oxo[3] ligands, without direct participation of the metal center. In a less common and less well-understood scenario, alkenes can react with *complex* (such as bidentate) ligands. The element sulfur is particularly prominent in ligand-based reactivity,[4,5] both in simple sulfides[4a,4b,4d] and in more complex[4c,4e,4f,5] ligands. The group 10 metal bisdithiolenes, $M(S_2C_2R_2)_2$ (M = Ni, Pd, Pt), were among the first metal complexes to demonstrate ligand-centered reactivity toward both monoolefins and 1,3-dienes.[5] Although this reactivity was discovered decades ago, the field is far from being mature. Potential industrial applications were suggested comparatively recently (2001),[5j] but applications will require a better understanding of the fundamental reactivity.

Theoretical studies[6] have shed some light on the reactions of unsaturated hydrocarbons with metal bisdithiolenes, although experimental findings continue to provide surprises. For reactions between alkenes and metal bisdithiolenes, intraligand alkene addition was initially proposed (Scheme 1a),[5a,5b] Such reactivity would be in line with expectations based on frontier orbitals.[6a,7]

Yet, subsequent characterization[5c,5d] (including an X-ray structure[5c]) of stable metal bisdithiolene adducts of nonconjungated dienes (reacting as monoolefins) revealed symmetry-forbidden *interligand* binding of the organic substrates (Scheme 1b), thus casting doubt on the utility of frontier molecular orbital (MO) analysis for predicting metal bisdithiolene reactivity. However, recent results have contributed to the reestablishment of the validity of MO analysis[8] for metal bisdithiolene reactivity: very pure $Ni(tfd)_2$ [tfd = $S_2C_2(CF_3)_2$] reacts with alkenes (in rigorously purified/dried solvents) according to the Woodward−Hoffmann rules, giving symmetry-allowed intraligand addition (Scheme 1a), while the symmetry-forbidden interligand addition pathway (Scheme 1b) is mediated, in impure samples, by the odd-electron species $[Ni(tfd)_2]^-$.[5m] Also, MO arguments were

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(7) See ref 6b for Kohn−Sham MO of $Ni(S_2C_2Me_2)_2$. The depiction of the lowest unoccupied MO in Scheme 1 omits, for clarity, the small metal-based atomic orbital contribution.

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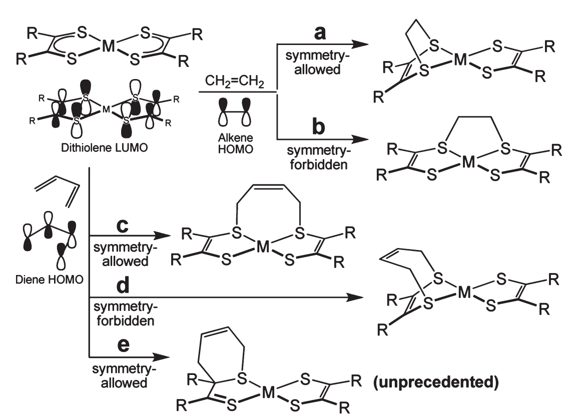
Scheme 1



recently applied to the alkene reactivity of metal *trisdithiolenes*, correctly predicting symmetry-allowed intraligand addition.[4c] Thus, frontier orbital arguments,[5f,5i,5m,6a] based on a spin-restricted ("closed-shell") picture, are extremely useful for predicting the reactivity of metal dithiolene complexes, despite the possibility of some singlet diradical ("open-shell") character for certain metal dithiolene complexes.[6c,9]

The reactivity of square-planar metal bisdithiolenes with 1,3-*dienes* has received less attention than the reactivity with monoolefins and deserves to be revisited. Some conceivable reactions are shown in Scheme 1c−e. Only reactions of type c (Scheme 1) have been observed so far.[5e−5g] To enhance the metal complex stability, we decided to study the platinum complex Pt(tfd)$_2$ (complex **1**) in 1,3-diene binding reactions. Our findings are surprising and will likely prove useful for applications (see below).

The reaction of Pt(tfd)$_2$ with excess 2,3-dimethyl-1,3-butadiene was studied by NMR spectroscopy. The reaction between Pt(tfd)$_2$ (ca. 10 mM in C_6D_6) and excess (4 equiv) diene is complete within less than 10 min at room temperature. S,S-Interligand addition is allowed by orbital symmetry (Scheme 1c), and an interligand adduct (complex **2**) is indeed observed, unambiguously assigned by ^{19}F NMR (Figure 1, top) and ^{1}H NMR spectroscopy.[10] The ^{1}H NMR spectrum is similar to the reported spectrum[5e] of the 2,3-dimethyl-1,3-butadiene adduct (interligand fashion) of the analogous nickel complex, Ni(tfd)$_2$, which has been crystallographically characterized.[5f] A 1,3-diene (cyclohexa-1,3-diene) adduct of the palladium complex Pd($S_2C_2Ph_2$)$_2$ exhibits an analogous structure.[5g] Utilizing an internal standard having both hydrogens and fluorines [3,5-bis(trifluoromethyl)bromobenzene, BTBB], we confirmed 1:1 stoichiometry for the rapidly formed initial adduct **2**. However, a small amount of a new compound (complex **3**) can be seen already (Figure 1, top). Conversion to the new species is complete after 20 h at 50 °C (Figure 1, bottom).

NMR integration versus the internal standard BTBB shows that in **3** *two* dienes bind to one metal complex. Valuable structural information is obtained from ^{19}F NMR spectroscopy:[11] In diene adducts **2** and **3**, the original high symmetry of **1** (D_{2h}) is lost, such that two sets of nonequivalent ^{19}F NMR signals (each corresponding to two CF_3 groups) are observed for each complex. In compound **2**, where the two CF_3 groups within a $F_3C-CC-CF_3$ subunit are nonequivalent, the fluorine signals occur as quartets ($^5J_{F-F}$ = 12.7 Hz; Figure 1, top). In contrast, for compound **3**, the two CF_3 groups in each $F_3C-CC-CF_3$ substructure are equivalent, as seen from the fact that the ^{19}F NMR spectrum for **3** shows two singlets; if the two CF_3 groups on each $F_3C-CC-CF_3$ unit were nonequivalent, quartets (as seen for **2**) would be expected because of their close van der Waals contacts,[12] while F−F coupling is not observed between CF_3 groups on separate $F_3C-CC-CF_3$ units. It is therefore concluded that both dienes have added to one tfd ligand in complex **3**. For complex **3**, one set of fluorines is clearly coupled to ^{195}Pt (12.6 Hz, expanded view in Figure 1, bottom), while the F−Pt coupling is too small to be detected for the other resonance. The signal showing F−Pt coupling can reasonably be assigned to the intact dithiolene ligand, and the signal lacking Pt satellites should be attributed to the comparatively weakly bound bisthioether ligand formed by double diene addition.

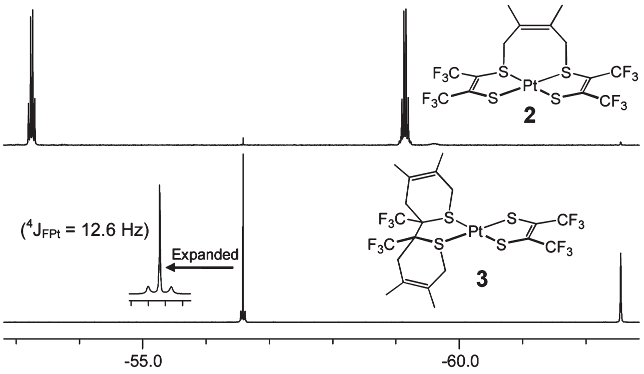


Figure 1. ^{19}F NMR spectra for a reaction mixture involving **1** (5 μmol) and excess 2,3-dimethyl-1,3-butadiene (20 μmol) in C_6D_6 (ca. 0.5 mL). Top: ca. 7 min after mixing (reaction at room temperature), **2** is observed and a trace of **3** is already visible. Bottom: after heating to 50 °C for 20 h, complete conversion to **3** has occurred.

Crystals of **3** (as a benzene solvate) were grown from a concentrated solution in C_6H_6 at 12 °C, and an X-ray crystallographic structure determination was carried out.[13] The result (Figure 2) is fully consistent with solution NMR data and yields valuable additional information: the symmetry element retained is not a mirror plane but a C_2 axis. Two

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[9] A singlet diradical (dithiyl) ground state has been proposed for [Ru(DPPBT)$_3$]$^+$ ([DPPBT]$^-$ = 2-diphenylphosphinobenzenethiolate), which undergoes ligand-based reactions with alkenes. See ref 4e.

[10] NMR data for **2**: ^{1}H NMR (400.0 MHz, C_6D_6, 298 K) δ 1.18 (6 H, s, CH_3), 3.06 (2 H, m, C*H*H′-C*H*H′), 3.32 (2 H, m, CH*H*′-CH*H*′); also present are free 2,3-dimethyl-1,3-butadiene [δ 1.84 (6 H, CH_3), 4.93 (2 H, m, olefinic H), 5.05 (2 H, m, olefinic H)] and BTBB internal standard [7.36 (2 H, s), 7.40, (1 H, s)]; ^{19}F NMR (376.5 MHz, C_6D_6, 298 K, using internal reference BTBB at δ −64.00; external reference trifluoroacetic acid appeared at δ −76.58) δ −59.11 (6 F, q, $^5J_{F-F}$ = 12.7 Hz, CF_3), −53.21 (6 F, q, $^5J_{F-F}$ = 12.7 Hz, CF_3).

[11] NMR data for **3**: ^{1}H NMR (400.0 MHz, C_6D_6, 298 K) δ 1.20 (6 H, s, CH_3), 1.35 (6 H, s, CH_3), 1.86 (2H, m, CH_2), 2.56 (2H, m, CH_2), 3.09 (4H, m, CH_2×2); ^{19}F NMR (376.5 MHz, C_6D_6, 298 K, BTBB internal reference) δ −62.52 (6 F, s, CF_3), −56.55 (6 F, s with Pt satellites, $^4J_{Pt-F}$ = 12.6 Hz, CF_3).

[12] Mallory, F. B.; Mallory, W. C. Coupling Through Space in Organic Chemistry. In *Encyclopedia of Nuclear Magnetic Resonance*; Wiley: New York, 1996.

[13] X-ray crystallographic data for **3** (benzene solvate): data collection on a Nonius-Kappa CCD diffractometer using Mo Kα (0.710 73 Å) at 150(1) K, structure solution with direct methods and refinement on F^2 against all reflections. Crystal data and structure refinement: greenish-yellow needle, crystal size = 0.10×0.04×0.03 mm, $C_{26}H_{26}F_{12}Pt_1S_4$, M = 889.80, monoclinic, space group $C2/c$, a = 13.2761(5) Å, b = 16.6218(9) Å, c = 14.4963(5) Å, β = 110.297(2)°, Z = 4, V = 3000.3(2) Å^3. D_{calc} = 1.970 g cm^{-3}, 11 556 reflections collected, of which 3437 were independent, GOF = 1.038, R1 = 0.0429 [data with $I > 2\sigma(I)$], wR2 = 0.0856 (all data).

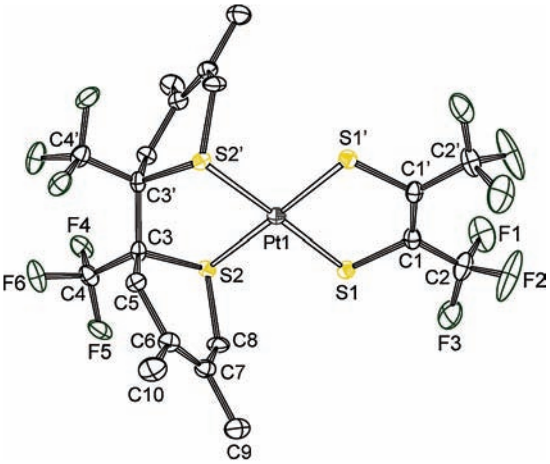


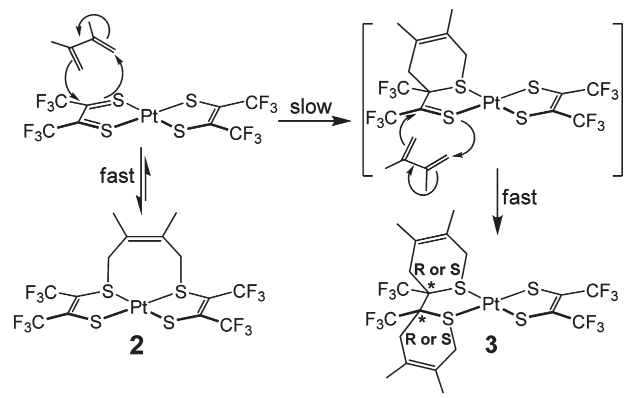
Figure 2. Structure of **3**, using 30% thermal ellipsoids. Hydrogen atoms are not shown, for clarity. Primed atoms are related to corresponding nonprimed atoms by a crystallographic 2-fold rotation axis. Selected distances and angles (Å, deg): Pt1−S1, 2.260(2); Pt1−S2, 2.302(1); S1−C1, 1.761(6); S2−C8, 1.814(5); S2−C3, 1.865(6); C1−C1′, 1.34(1); C3−C3′, 1.58(1); C3−C5, 1.564(6); C5−C6, 1.517(7); C6−C7 1.315(8); C7−C8, 1.493(7); S1−Pt1−S1′, 89.45(8); S2−Pt1−S2′, 88.81(7).

dienes have added to the same tfd ligand in C,S-intraligand (compare Scheme 1e) fashion. While this binding mode is unprecedented for dithiolenes,[14] it is in accordance with frontier orbital expectations (Scheme 1).

The reaction that gives **3** is high-yielding (quantitative conversion by NMR, 81% isolated yield on a 0.1 g scale) and shows complete stereoselectivity, yielding exclusively the C_2-symmetric isomer, which possesses a new chiral chelating bisthioether ligand. While the C_2-chiral ligand itself has two stereogenic centers (C3 and C3′ in Figure 2), complex **3** has two additional stereocenters due to chirality at the metal-coordinated sulfur atoms (S2 and S2′).

While the configuration at sulfur may conceivably be under thermodynamic control once the configuration at carbon is given (the observed structure minimizes ring strain), it would also be the configuration expected from a mechanism involving concerted *syn*-facial addition of the diene across the CS bond. The diastereoselectivity that governs the formation of a single C_5S_1 six-membered ring is thus somewhat expected for a hetero-Diels−Alder reaction. However, the observation of only one diastereomer of **3** is very remarkable because *two* C_5S_1 rings have formed in **3**. Such a structure may be either a C_s-symmetric meso isomer or a C_2-symmetric chiral isomer, depending on the configurations of the stereocenters within one C_5S_1 ring relative to the other ring. Only the C_2-chiral isomer is observed. A proposed mechanism for the formation of **3** is shown in Scheme 2. The initial binding of 2,3-dimethyl-1,3-butadiene to Pt(tfd)$_2$ (**1**) to yield **2** is reversible, which we directly observed by NMR spectroscopy: using a dilute (ca. 1 mM or less) solution of **2** having only a small excess of diene, both **2** and a small amount of **1** were observed in equilibrium. The formation of **2** from **1** and 2,3-dimethyl-1,3-butadiene is associated with an equilibrium constant $K = 9(2) \times 10^3$ M^{-1} (in C_6D_6 at 296 K; Supporting Information).[15] It is reasonable to expect that diene dissociates from **2** and then forms a highly reactive monodiene C,S-adduct (Scheme 2, structure in square brackets). The latter should be highly reactive because of very pronounced thioketone character, but attack of the second diene should occur at the sterically more accessible side, forming C_2-symmetrical **3**. In contrast to the reversibility for the formation of **2**, the formation of **3** is irreversible under the conditions we examined (no diene was lost in the dilute solution or upon prolonged exposure to vacuum at room temperature).

Scheme 2



Chiral chelating bisthioethers are useful for several enantioselective reactions, most prominently allylic substitutions.[16] Achieving high yields of a C_2-chiral ligand instead of the C_s-symmetrical meso diastereomer is not trivial, and our newly discovered highly diastereoselective bisdiene addition thus appears very promising for applications in ligand synthesis. Future work in our group will concentrate on obtaining the new chiral ligand in its free form and on synthesizing this ligand and related ligands in nonracemic form, for applications in catalysis.

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Supporting Information Available: Crystallographic data for **3** (CIF) and supporting text containing experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Considering that CS bonds in Pt($S_2C_2R_2$)$_2$ have some thioketone character, it is relevant that free diarylthioketones undergo hetero-Diels−Alder additions with 1,3-dienes (likely concerted for very reactive dienes but apparently stepwise for less reactive dienes): Wilker, S.; Erker, G. *J. Am. Chem. Soc.* **1995**, *117*, 10922.

(15) A value extremely similar to that for the corresponding nickel system, where ref 5e reports 1.1×10^4 M^{-1} at 298 K in a hydrocarbon solvent.

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