

The Modulating Possibilities of Dicarbollide Clusters: Optimizing the Kharasch Catalysts

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The structurally and coordinatively similar dicarbollide [7,8-C₂B₉H₁₁]²⁻ (Dcb)¹ and cyclopentadienyl ligands [C₅R₅]⁻ (Cp[#])¹ differ in their capacity to stabilize high oxidation states and the out-of-plane disposition of the open-face substituents.^{1,2} These differences offer new alternatives in fields where Cp is a basic participant and in which association/dissociation of ligands³ and electron capture/release are key steps. In the Kharasch reaction, also known as atom transfer radical Addition (ATRA),⁴ the above-mentioned steps are fundamental. This is why ATRA reaction was chosen to compare Dcb and Cp options. To date some of the more active ATRA catalysts contain Cp-like ligands, e.g., [RuClCp[#]-(PPh₃)₂] (Cp[#] = Cp (**1**), Cp* (**2**), and indenyl (**3**)).^{4b,5} Substitution of one open-face hydrogen by a SR₂ in Dcb leads to the new monoanionic dicarbollide, [R₂S-7,8-C₂B₉H₁₀]⁻. We have chosen the most symmetrical position to locate the R₂S group, although other positions are also possible,⁶ and [10-R¹R²S-7-R-7,8-C₂B₉H₉]⁻ (**4a-f**) derivatives were synthesized.⁷ Reaction of these ligands with [RuCl₂(PPh₃)₃] in ethanol led to complexes with the [3-H-3,3-(PPh₃)₂-8-SR¹R²-1-R-3,1,2-RuC₂B₉H₉] (**5a-f**) general stoichiometry (Scheme 1). All complexes **5a-f**, were characterized by NMR techniques, and the structure of **5a** (Figure 1) was determined by X-ray structure analysis. Crystals of **5a** were grown from a solution of CH₂Cl₂/hexane.

The ¹¹B NMR spectra of complexes with R = H and R¹ = R² (**5a**, **5b**, **5d**) display a 1:1:1:3 pattern in agreement with C_s symmetry. The crystal structure determination of **5a** [3-H-3,3-(PPh₃)₂-8-SMe₂-3,1,2-RuC₂B₉H₁₀] unambiguously indicates that the metal hydride points toward sulfur (Figure 1). Bond distances of **5a** are very similar to those of the noncompensated anion [3-H-3,3-(PPh₃)₂-3,1,2-RuC₂B₉H₁₁]⁻ (**6**),⁸ Ru-P (2.321(3) and 2.298(3) Å vs 2.322 and 2.294 Å), and the P-Ru-P angle has the same value 96.1(1)°. The Ru distance to the C₂B₃ open face is 1.735(5) Å for **5a** and 1.771 Å for **6**. The Ru-B and Ru-C distances in **5a** are very similar, ranging from 2.203(11) to 2.307(10) Å. Therefore the pendant R₂S⁺ group has not produced significant geometric changes in the complex. In support of this is the similar angle between the B(8)-S and the C₂B₃ plane for **5a** (14.2°) and **4a** (17.1°).⁷ This implies that in the event one PPh₃ should dissociate, the long 3.435(3) Å S-Ru distance in **5a**, larger than the van der Waals radii, should prevent a S-Ru contact.

The Kharasch addition of CCl₄ to methyl methacrylate (MMA) and styrene (Sty) double bonds has been examined to compare the catalytic activity of **5a-f** with **2**, which is considered to be the fastest and highest Kharasch conversion capacity Ru complex.^{4b} All **5a-f** complexes are superior in all aspects to **2**, as shown in Table 1.

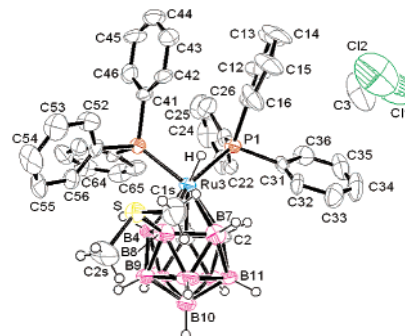


Figure 1. Molecular structure of **5a**·CH₂Cl₂ showing the atom-labeling scheme.

Scheme 1. Preparation of Complexes **5a-f**

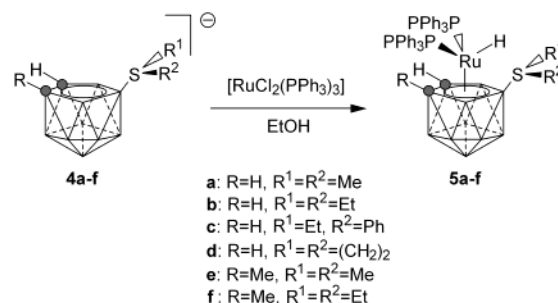


Table 1. Cyclic Voltammetry^a Data and Kharasch Addition of Carbon Tetrachloride to Styrene and Methyl Methacrylate^b

ΔE [mV]	E [mV]	catalyst	conversion ^c [%]/yield ^c [%]	
			styrene	MMA
86	+133	1	24/10	62/5
94	-83	2	86/69	79/79
94	-10	3	74/69	83/83
76	-266	5a	100/99	98/94
82	-266	5b	100/99	98/94
98	-287	5c	100/99	100/100
80	-266	5d	100/99	99/99
80	-366	5e	100/99	92/84
88	-368	5f	100/99	92/84

^a Sample, 1 mM; Bu₄NPF₆ (0.1 M) in CH₂Cl₂; ν = 50 mV s⁻¹; potentials are reported in millivolt versus ferrocene as an internal standard. ^b Reaction conditions: olefin (9 mmol), carbon tetrachloride (13 mmol), catalyst (0.03 mmol), toluene (4 mL), dodecane (0.25 mL), under nitrogen atmosphere. The reactions were carried out at 40 °C and stopped after 6 h. ^c Conversions and yields are based on the olefin, and determined by GC using dodecane as internal standard. The Kharasch adducts were characterized by comparison with literature data.^{4b}

In particular for **5c** and with regard to MMA and Sty, total turnover numbers (TTN) of 4200 and 9000, and initial turnover frequencies (TOF) of 1880 and 1500 h⁻¹ were obtained at 40 °C,

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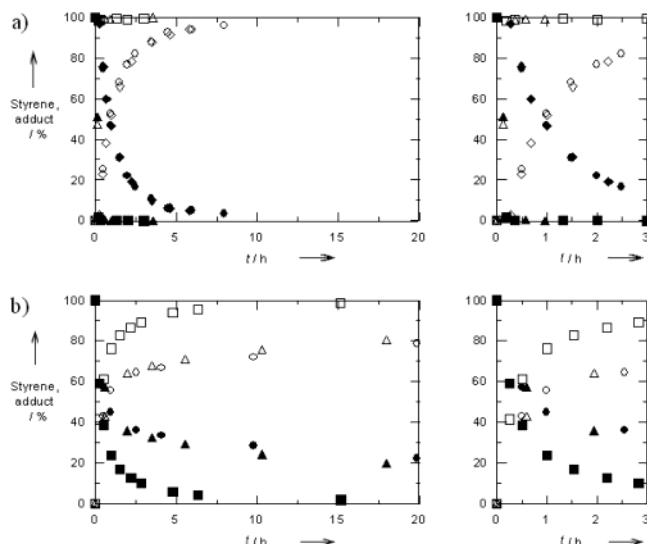


Figure 2. Styrene (■,●,▲,◆) and adduct (□,○,△,◇) vs time for the Kharasch addition of CCl_4 to styrene at 40°C catalyzed by complexes **5a**, **5c**, and **2** without PPh_3 and in the presence of 12 equiv of PPh_3 . (a) Complex **5a** without PPh_3 (■,□) and with 11.9 equiv of PPh_3 (●,○); complex **5c** without PPh_3 (▲,△) and with 12.1 equiv of PPh_3 (◆,◇). (b) **2** without PPh_3 (■,□), with 12.05 (▲,△) and 12.4 equiv of PPh_3 (●,○).

respectively, as opposed to maximum TTN of 1600–1700 and TOF of 400 h^{-1} observed for **2**.^{4b} In addition, the TTN for **5c** is even higher than the one obtained for the pincer N,C,N-chelating aryldiaminonickel complex, to this moment the most efficient ATRA catalyst reported, with TTN of 1730 and TOF of 400 h^{-1} for MMA.⁹ With the superior reactivity of **5c** for this type of reaction, it remained to be determined whether it is due to: (i) the capacity of R_2S^+ to donate two electrons to the metal after dissociation of one phosphine; (ii) the fine-tuning to optimal potential in the Ru catalyst made by $[\text{10-R}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10}]^-$, or (iii) a combination of both.

Point (i) was addressed by adding free PPh_3 to the reaction mixture, reasoning that addition of phosphine would decrease the rate dramatically, as observed in reactions in which a phosphine dissociative pathway is operative.^{4a,10,11} Addition of up to 12 equiv of PPh_3 per equiv of catalyst in reactions catalyzed by **5a** and **5c** slowed the reaction rate (Figure 2a) in a manner parallel to that with **2** (Figure 2b). Complex **2** does not have the capacity to internally satisfy the electronic demands of a complex having lost one ancillary ligand. With the behavior of **5a/5c** parallel to that of **2**, we considered that the stabilizing capacity of the R_2S^+ group on the ligand's dissociation could be discounted, in agreement with the structural data discussed earlier.

Possibility (ii) was addressed correlating the E° values for the $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ process with the catalytic Kharasch activity toward a common substrate. Cyclic voltammetry data are displayed in Table 1. On the basis of these data, the catalyst activity order is **5a–d** > **5e–f** > **2,3** > **1**. Interestingly, groupings of catalysts can be made, both from the catalytic activity side, and from the E° point of view. In this way, **5a–d** have E° 's near -270 mV and are the most active catalysts; close in activity are **5e** and **5f** with E° 's near -370 mV .

Consequently, catalyst precursors with E° 's near -370 mV are not as efficient as these with E° 's near -270 mV , but all of them are more efficient than **2**, **3**, and **1** with E° 's between -83 mV and $+133\text{ mV}$. The fact that the highest catalytic activity is found neither at one extreme of E° 's values nor the other, but between, implies that both species, Ru^{II} and Ru^{III} , must be equally stabilized by the same ligand system and that for a maximum efficiency of the catalytic conversion process E° must be in a narrow range of potentials. In this way **2** and **3** are more efficient than **1**, confirming that the closer to -270 mV is E° , the best for maximum catalytic performance. This proves that a direct relationship between ATRA catalyst efficiency and E° does exist for these complexes.

Charge-compensated carborane ligands have thus allowed the adequate tuning of the E° values of the $\text{Cp}^\#$ ligands, permitting the necessary potential to be reached through *exo*-cluster substitution. It is our interpretation that this has been possible through a to-and-fro electron density movement, facilitated by the uniqueness of the boron cluster–sulfonate bridge. We believe that the capacity to donate and to retrieve electron density from the metal makes the $[\text{10-R}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10}]^-$ system very adequate when two oxidation states are required to be stabilized by the same ligand system in different steps of a catalytic process.

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Supporting Information Available: Crystallographic data (CIF) and X-ray structure details (PDF) of **5a**· CH_2Cl_2 . This material is available free of charge via the Internet <http://pubs.acs.org>.

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