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Observations on Regioselectivity During the Addition of Carbon Nucleophiles to Isoprene-Mo(CO)$_2$Tp Cationic Complex

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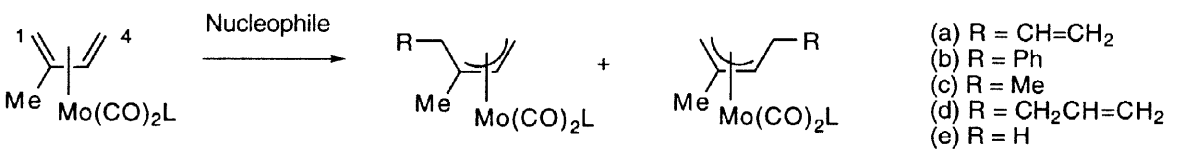
Abstract: Addition of carbon nucleophiles, such as phenylmagnesium bromide, to isoprene-Mo(CO)$_2$Tp (Tp = hydridotris(1-pyrazolyl)borato), can proceed with excellent regiocontrol, predominantly at the diene terminus remote from the 2-methyl substituent. In contrast to the corresponding cyclopentadienyl complex, their is no reversal of regiochemistry as a result of solvent effects.

We recently described reactions of isoprene-Mo(CO)$_2$Cp (**1**) with a range of carbon and hydride nucleophiles, in which regioselectivity was found to be a function of the solvent and/or additives used for the reaction.[1] Thus, treatment of **1** with phenyllithium in diethyl ether at 0 °C afforded an 80:20 mixture of complexes **2** and **3**, resulting from predominant nucleophile addition at the sterically more hindered diene terminus (proximal to the methyl substituent). The same reaction conducted in tetrahydrofuran as solvent afforded a 50:50 mixture of **2** and **3**, at 0 °C, and a 30:70 mixture at -78 °C. Inclusion of a complexing agent (HMPA or TMEDA) in the reaction in ether led to a reversal of selectivity (TMEDA: 20:80 ratio of **2**:**3**; HMPA: 30:70), and in THF an increase in the preference for the C(4) adduct (HMPA: 15:85 at 0 °C). Similar observations were made when PhMgBr, MeMgBr, allylMgBr, or vinylMgBr were used as the nucleophiles. In contrast, hydride nucleophiles ($LiBH_4$, $NaBH_3CN$) showed a preference for C(1) attack regardless of solvent.[1,2]



1 L = Cp **2** L = Cp **3** L = Cp

4 L = Tp **5** L = Tp **6** L = Tp

Owing to the fact that compounds of structure **3** were found to be photo labile and difficult to purify, characterize, and utilize in further transformations, whereas the corresponding π-allyl-Mo(CO)$_2$Tp complexes (Tp = hydridotris(1-pyrazolyl)borato[3]) appear to be much more stable and relatively easy to handle,[4] we have studied the corresponding reactions of complex **4** with carbon and hydride nucleophiles in an effort to secure materials that are more user-friendly. We also anticipated that the bulky Tp ligand may have a significant effect

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on the chemistry of the diene system itself, as is indeed shown by the results outlined in the present communication.

Complex **4** has been reported by us previously,[5] and was prepared in high overall yield from 3-methyl-2-butenyl bromide, by a three-step procedure. Our earlier report described the reactions of **4** with enolate nucleophiles, which generally give mixtures of **5** and **6** favoring the latter (*ca.* 1:2). Complex **4** was found to be completely unreactive to PhLi in ether at -78 °C (Table, entry 1), and gave unidentifiable mixtures of multiple products on reaction with PhLi in THF at -78 °C (entry 2), or in Et_2O at rt (entry 3). In contrast, the reactions of **4** with Grignard reagents all proceeded satisfactorily at rt, and the results for all reactions studied are given in the Table.[6]

Table: Results of nucleophilic addition reactions on complex **4.**

Entry	Nucleophile	Reaction Conditions	Yield(%)	Ratio **5:6**
1	PhLi	Et_2O, -78 °C, 1.5 h	N/A	95% SM recovered
2	PhLi	THF, -78 °C, 1.5 h	N/A	unidentifiable complexes (40% SM recovered)
3	PhLi	Et_2O, rt, 3h	N/A	unidentifiable complexes
4	VinylMgBr	Et_2O, -78 °C, 2 h	N/A	SM recovered
5	VinylMgBr	Et_2O, 0 °C, 3 h	97	30:70
6	VinylMgBr	Et_2O, rt, 0.5 h	92	40:60
7	VinylMgBr	CH_2Cl_2, rt, 0.75 h	99	20:80
8	VinylMgBr	THF, rt, 1 h	99	10:90
9	VinylMgBr	THF, 2 equiv TMEDA, rt, 0.5h	90	5:95
10	PhMgBr	Et_2O, -78 °C, 2 h	N/A	SM recovered
11	PhMgBr	Et_2O, rt, 1 h	94	25:75
12	PhMgBr	THF, rt, 0.5 h	99	20:80
13	PhMgBr	THF, 2 equiv TMEDA, rt, 0.5h	80	5:95
14	MeMgBr	THF, rt, 1 h	88	10:90
15	AllylMgBr	THF, rt, 0.75 h	70	45:55
16	AllylMgBr	THF, 2 equiv TMEDA, rt, 0.75h	68	40:60
17	$NaBH_4$	THF, rt, 0.5 h	99	50:50
18	$LiAlH_4$	THF, rt, 0.5 h	97	45:55
19	$NaBH_3CN$	THF, rt, 6 h	99	40:60
20	L-Selectride	THF, rt, 0.5 h	50	45:55
21	Super-Hydride	THF, rt, 0.5 h	20	40:60

Immediately apparent is the observation that under no conditions do we observe a preference for the addition of nucleophile at C(1), the sterically more hindered diene terminus. However, the enhanced preference for the C(4) adduct upon the addition of complexing agents is still observed (entries 9, 13, 16 vs. 8, 12, 15, respectively), as is the increase in C(4) adduct formation when the reaction is performed in THF vs. Et_2O (entry 8 vs. 6). Indeed, excellent regiocontrol can be obtained by using a combination of THF and TMEDA, provided

one targets the product π-allyl complex **6** (entries 9 and 13). Allylmagnesium bromide does not show a marked change, probably because reactions of this system occur at the non-metallated allyl terminus, the steric demand of which is less sensitive to the solvation sphere of the metal. Again in contrast to the reactions of complex **1**, addition of hydride gave rather poor regiocontrol (entries 17 - 21). All of the results are indicative of a stronger preference for C(4) addition to the Tp complex **4** compared with the Cp derivative **1**.

In considering the possible explanations for this regiochemistry, we are cognizant of the recent results from the laboratories of Liebeskind[4(b)] and Sarkar[7] that indicate a thermodynamic preference for π-allyl-$Mo(CO)_2Tp$ complexes that have terminal *anti* substituents (i.e., with the stereochemistry shown for the CH_2R substituent of complex **6**) versus terminal *syn* substituents (stereochemistry shown for the methyl group of complex **5**). It is likely that this preference arises from non-bonded interactions between the *syn* substituent and a proximal equatorial pyrazole ring of the Tp ligand, in the major conformation of the allyl complex.[8] This destabilizing influence of the *syn* methyl on complexes **5** would result in a preference for the formation of **6**, provided the transition state for the nucleophile addition is product-like. Such an interaction would be absent, or much reduced, in the corresponding Cp complexes, so that a very different scenario would ensue during conversion of the diene complex **1** to its nucleophile addition products.

All of the π-allyl-$Mo(CO)_2Tp$ complexes reported here were found to be quite stable and easy to handle during routine procedures, thereby giving them a considerable advantage over the cyclopentadienyl analogs. In conjunction with our recent disclosure[5] of methodology for the conversion of both types of π-allyl complex (**5** and **6**, R = CH_2CO_2H) to functionalized alkenes, by demetallation, the regiocontrol shown for carbon nucleophiles is expected to provide useful approaches for the construction of stereodefined olefinic systems.

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(6) All new compounds were purified by flash chromatography and characterized by IR, ^1H and ^{13}C NMR spectroscopy, and high resolution mass spectrometry. Data for representative examples:
Complex **5a**: R_f 0.09 in hexane/methylene chloride (12:1); IR ($CHCl_3$) ν_{max} 1842, 1936, 2242 cm^{-1}; ^1H NMR ($CDCl_3$); δ 7.85 (3H, broad, Tp), 7.55 (3H, broad s, Tp), 6.20 (3H, broad s, Tp), 5.70 (1H, m,

olefin), 5.05 (2H, m, olefin), 3.91 (1H, dd, H^2, J = 9.9, 7.0 Hz), 3.57 (1H, dd, *anti*-H^1, J = 7.0, 4.7 Hz), 2.72 (1H, dd, *anti*-H^4, J = 14.6, 7.6 Hz), 1.90 (3H, s, Me), 1.85 (1H, dd, *syn*-H^1, J = 9.9, 4.7 Hz), 1.43 (1H, dd, *syn*-H^4, J = 14.6, 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 230.2 (CO), 233.2 (CO), 146.1(Tp), 138.9 (olefin), 135.5 (Tp), 115.9 (olefin), 105.3 (Tp), 99.63 (C-3), 81.4 (C-2), 48.0 (C-1), 42.3 (allylic), 25.8 ($\underline{C}H_3$); HRMS calc'd for $C_{16}H_{21}BN_6Mo(^{98}Mo)$ for [M^+-2(CO)] 406.0976, found 406.0955. **6a**: R_f 0.16 (hexane/methylene chloride, 12:1); IR ($CHCl_3$) ν_{max} 1858, 1946, 2242 cm^{-1}; ^1H NMR ($CDCl_3$); δ 8.48 (1H, d, Tp, J = 1.9 Hz), 7.97 (1H, d, Tp, J = 1.9 Hz), 7.90 (1H, d, Tp, J = 1.9 Hz), 7.57 (2H, d, Tp, J = 1.9 Hz), 7.44 (1H, d, Tp, J = 1.9 Hz), 6.20 (3H, m, Tp), 5.85 (1H, m, C($\underline{H}$)=CH_2), 5.05 (2H, m, C(H)=C$\underline{H_2}$), 4.05 (1H, dd, H^3, J = 10.4, 7.4 Hz), 3.49 (1H, d, *anti*-H^1, J = 1.8 Hz), 2.85 (1H, m, *anti*-H^4), 1.97 (1H, d, *syn*-H^1, J = 1.8 Hz), 1.54 (3H, s, C$\underline{H_3}$), 1.02 (1H, m, *syn*-H^4); ^{13}C NMR ($CDCl_3$) δ 228.0 ($\underline{C}$O), 226.9 ($\underline{C}$O), 147.1(Tp), 142.5 (Tp), 142.3 (Tp), 140.7 (Tp), 136.1 (Tp), 134.0 (Tp), 114.3 ($\underline{C}$(H)=CH_2), 105.6 (C(H)=$\underline{C}H_2$), 105.1 (Tp), 82.4 (C-2), 72.3 (C-3), 55.9 (C-1), 36.6 (C-4), 20.6 (Me); HRMS calc'd for $C_{16}H_{21}BN_6Mo$ (^{98}Mo) for [M^+-2(CO)] 406.0976, found 406.0972.
5b: R_f 0.14 (hexane/methylene chloride, 2:1); IR ($CHCl_3$) ν_{max} 1852, 1945, 2255 cm^{-1} ; ^1H NMR ($CDCl_3$); δ 7.8-8.0 (3H, broad, Tp), 7.56 (3H, broad s, Tp), 7.27 (5H, m, Ph), 6.21 (3H, broad s, Tp), 3.95 (1H, dd, H^2, J = 9.8, 7.2 Hz), 3.72 (1H, dd, *anti*-H^3, J = 7.2, 3.9 Hz), 3.25 (1H, d, *anti*-H^4, J = 14.2 Hz), 2.05 (1H, dd, syn-H^3, J = 9.8, 3.9 Hz), 2.00 (1H, dd, *syn*-H^4, J = 14.2 Hz), 1.72 (3H, s, Me); HRMS calc'd for $C_{22}H_{23}BN_6O_2Mo$ (^{98}Mo) 512.1030, found 512.0993, calc'd for [M^+-2(CO)] 456.1132, found 456.1150. **6b**: R_f 0.26 (hexane/methylene chloride, 2:1); IR ($CHCl_3$) ν_{max} 1852, 1944, 2254 cm^{-1}; ^1H NMR ($CDCl_3$); δ 8.50 (1H, broad s, Tp), 7.97 (1H, d, Tp, J = 2.2 Hz), 7.86 (1H, d, Tp, J = 2.2 Hz), 7.59 (1H, d, Tp, J = 2.2 Hz), 7.57 (1H, d, Tp, J = 2.2 Hz), 7.45 (1H, d, Tp, J = 2.2 Hz), 7.27 (5H, m, Ph), 6.24 (1H, t, Tp), 6.21 (1H, t, Tp), 6.15 (1H, t, Tp), 4.21 (1H, ddd, H^3, J = 13.0 11.5, 2.9 Hz), 3.58 (1H, d, *anti*-H^1, J = 2.0 Hz), 3.39 (1H, dd, *anti*-H^4, J = 11.5, 3.3 Hz), 2.16 (1H, d, syn-H^1, J = 2.0 Hz), 1.58 (1H, d, *syn*-H^4, J = 13.0, 3.3 Hz), 1.47 (3H, s, Me); ^{13}C NMR (CD_3CN) δ 147.1, 142.5, 142.4, 136.2, 134.1, 128.4, 126.0, 105.7, 105.1, 82.0, 74.5, 55.9, 38.1, 20.8; HRMS calc'd for $C_{22}H_{23}BN_6O_2Mo$ (^{98}Mo) 512.1030, found 512.1016, calc'd for [M^+-2(CO)] 456.1132, found 456.1128.

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