Table VII. Elements of the Exchange Matrix for the W-FPF_5 NMR Multiplet for Ionic Intramolecular Exchange in **3**

site	ν^a	spin state[b]	pop.[c]	transition probabilities[d]
1	-2190.37	$\alpha(\alpha^4)\alpha$	1	1 (1)
2	-1693.51	$\beta(\alpha^4)\alpha$	1	2 (1/6), 3 (1/6), 4 (4/6)
3	-1426.41	$\alpha(\alpha^4)\beta$	1	2 (1/6), 3 (1/6), 4 (4/6)
4	-1410.39	$\alpha(\alpha^3\beta)\alpha$	4	2 (1/6), 3 (1/6), 4 (4/6)
5	-929.55	$\beta(\alpha^4)\beta$	1	5 (1/15), 6 (4/15), 7 (4/15), 8 (6/15)
6	-913.53	$\beta(\alpha^3\beta)\alpha$	4	5 (1/15), 6 (4/15), 7 (4/15), 8 (6/15)
7	-646.43	$\alpha(\alpha^3\beta)\beta$	4	5 (1/15), 6 (4/15), 7 (4/15), 8 (6/15)
8	-630.41	$\alpha(\alpha^2\beta^2)\alpha$	6	5 (1/15), 6 (4/15), 7 (4/15), 8 (6/15)
9	-149.57	$\beta(\alpha^3\beta)\beta$	4	9 (4/20), 10 (6/20), 11 (6/20), 12 (4/20)
10	-133.55	$\beta(\alpha^2\beta^2)\alpha$	6	9 (4/20), 10 (6/20), 11 (6/20), 12 (4/20)
11	133.55	$\alpha(\alpha^2\beta^2)\beta$	6	9 (4/20), 10 (6/20), 11 (6/20), 12 (4/20)
12	149.57	$\alpha(\alpha\beta^3)\alpha$	4	9 (4/20), 10 (6/20), 11 (6/20), 12 (4/20)
13	630.41	$\beta(\alpha^2\beta^2)\beta$	6	13 (6/15), 14 (4/15), 15 (4/15), 16 (1/15)
14	646.43	$\beta(\alpha\beta^3)\alpha$	4	13 (6/15), 14 (4/15), 15 (4/15), 16 (1/15)
15	913.53	$\alpha(\alpha\beta^3)\beta$	4	13 (6/15), 14 (4/15), 15 (4/15), 16 (1/15)
16	929.55	$\alpha(\beta^4)\alpha$	1	13 (6/15), 14 (4/15), 15 (4/15), 16 (1/15)
17	1410.39	$\beta(\alpha\beta^3)\beta$	4	17 (4/6), 18 (1/6), 19 (1/6)
18	1426.41	$\beta(\beta^4)\alpha$	1	17 (4/6), 18 (1/6), 19 (1/6)
19	1693.51	$\alpha(\beta^4)\beta$	1	17 (4/6), 18 (1/6), 19 (1/6)
20	2190.37	$\beta(\beta^4)\beta$	1	20 (1)

[a] In Hz, relative to chemical shift of 0 Hz. [b] Listed in order of (μ-F)($F_{equatorial}$)$_4$(F_{axial}). [c] Actual population ×64. [d] For each line probability in parentheses of transition to the listed site. All other transition probabilities are zero.

the rate constant at 264.9 K on the basis of exclusive intramolecular exchange was determined to be 9000 s^{-1} and was used in the Eyring plot, but broadening from intermolecular exchange must be present so we have deleted this point here. In all cases, the error limits on the activation parameters were derived from the standard deviations of the slope and intercept of the least-squares fit straight line to the data.

The ionic exchange mechanism was treated as a 12-site exchange problem for the SbF_6^- and PF_6^- adducts and as an 8-site problem for BF_4^- adduct **2**. Elements of the exchange matrices are listed in Tables III and IV including the NMR exchange site number, frequency, fluorine spin state, population, and nonzero transition probabilities. The concerted mechanism for **2** is also an 8-site problem and as described in the text differs little from the ionic mechanism; elements of this exchange matrix are in Table IV. The concerted mechanism for the octahedral anions must be treated as a 24-site exchange problem since the axial, and cis- and trans-equatorial spin sites are in principle different; elements of this exchange matrix are in Table V. The intermolecular exchange mechanism, treated as described in the text, reduces to a 7-site problem for **1a**, **1b**, and **3**, and a 5-site problem for **2**, as shown in Table VI. Lastly, the calculation of the PF_6^- spectra in Figure 6 was treated as a 20-site exchange problem. Coupling constants from the ^{19}F NMR spectra of **3**[13b] ($J_{(\mu\text{-F})P}$ = 496.86 Hz, $J_{F(equatorial)P}$ = 779.98 Hz, and $J_{F(axial)P}$ = 763.96 Hz) were combined to give precise expected positions of a doublet of doublet of quintets, and elements of the exchange matrix are listed in Table VII.

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Catalysis of Diels-Alder Reactions by Low Oxidation State Transition-Metal Lewis Acids: Fact and Fiction

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Abstract: Catalysis of Diels-Alder reactions between the dienes cyclopentadiene, butadiene, isoprene, and piperylene and the enones acrolein, methyl vinyl ketone, and methyl acrylate is induced by 0.1-2.5 mol % of *mer*-(*cis*-Me_3P)(*trans*-NO)-$(CO)_3W(\mu\text{-F})SbF_5$ (**1**), $(Cy_2PCH_2CH_2PPh_2)(CO)_2(NO)W(\mu\text{-F})SbF_5$ (**2**), $Cp(CO)_2FeL^+X^-$ (L = THF, X^- = BF_4^-, **3a**; X^- = SbF_6^-, **3b**; L = η^1-acrolein, X^- = PF_6^-, **3d**), or $Cp(CO)_2L'ML^+PF_6^-$ (L' = CO, L = acrolein, M = Mo, **4a**; L' = PPh_3, L = THF, M = Mo, **4b**; L' = CO, L = THF, M = W, **4c**). Enhancement of rates and regio- and stereoselectivity is observed compared to the thermal reactions; the order of apparent catalytic activity is **1** > **2** ≈ **3a** > **4a**, **4c**. The order of Lewis acidity is **1** > **2** > **4a** > **3a**, casting doubt on the role of $Cp(CO)_2Fe^+$ in catalysis. The potential impurity $Ag^+BF_4^-$ is similarly reactive, although not in lower concentrations. Use of 2,6-di-*tert*-butylpyridine (**5**) and 1-(*n*-butyl)-2,2,6,6-tetramethylpiperidine (**6**) as hindered bases to trap Ag^+ and H^+ in the presence of transition-metal Lewis acids is described. Substoichiometric use of **5** demonstrates that $Ag^+BF_4^-$ is not the real catalyst and that the true activity of **3a** is low. Use of **5** with stronger acids, namely the acrolein adduct of **1** (**1a**) and **4a**, or of the stronger base **6** with **3a** leads to catalyst destruction, via a pathway proposed to involve deprotonation of coordinated methylene chloride. The reactivity of other potential impurities (HBF_4·Et_2O, BF_3·Et_2O, $Ph_3C^+PF_6^-$, and $NO^+SbF_6^-$) is briefly examined, as is that of analogues of **3a** that have different counterions. Kinetic analysis of stoichiometric reactions of metal-acrolein adducts with isoprene shows that the relative rates of cycloaddition for **1a**, the acrolein adduct of **2**, **4a**, and **3d** are 68:20:8:1 and that the rate-determining step in the catalytic reactions is the rate of aldehyde turnover. The calculated rate constants are used to predict catalytic yields and demonstrate that **1** and **2** can be the real catalysts. For **3a** and possibly **4a** as well, the observed catalytic activity is significantly greater than expected on the basis of the stoichiometrically determined rate constants, so the real catalysis in these cases apparently is due to the presence of much more reactive materials present as impurities.

We recently reported[1] that Diels-Alder reactions between butadiene or cyclopentadiene and α,β-unsaturated enones may be catalyzed by as little as 0.1 mol % of the tungsten nitrosyl Lewis acid $Me_3P(CO)_3(NO)W(\mu\text{-F})SbF_5$ (**1**)[2] and that the mode of catalysis is likely due to activation of the α,β-unsaturated enone by simple η^1-carbonyl coordination, on the basis of an X-ray structure of the tungsten-acrolein adduct **1a**. Since we were aware of related η^1-adducts of the metal fragments $Cp(CO)_2Fe^+$

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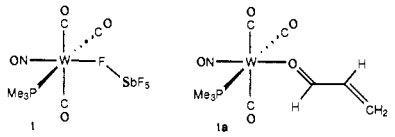


1 1a

and $Cp(CO)_3Mo^+$,[3] a more general investigation of the catalytic potential of such well-known[4] transition-metal Lewis acids seemed warranted. While we did not anticipate that these Lewis acids would necessarily have catalytic properties that would render them superior in terms of reaction rate, regioselectivity, or stereoselectivity to commonly used Diels–Alder Lewis acids,[5] the potential for designing catalysts capable of inducing *asymmetric* Diels–Alder reactions[6] seemed enormous. While such a chiral catalyst would not be required to be particularly reactive, in order for high enantioselectivity to be achieved the catalyzed reaction would at least have to be significantly faster than the thermal cycloaddition. However, since we anticipated that design of such a chiral Lewis acid might render its synthesis nontrivial and preclude the use of stoichiometric quantities, it probably would be required to be truly catalytic.[7] It was therefore important to investigate a range of transition-metal Lewis acids in order to determine the potential utility of such materials as catalysts and to investigate a variety of substituted dienes and dienophiles in order to define the scope of any catalytic reactions that were discovered. We report here the full details of our results with **1** and compare its reactivity with that of the related nitrosyl compound **2** and the cyclopentadienyl Lewis acids $Cp(CO)_2Fe(L)^+X^-$ (**3**) and $Cp(CO)_2(L')M(L)^+PF_6^-$ (**4**). Attention will be focused on **1**, which will be shown to be the most active catalyst, and on **3a** and **3d**, the cation of which is the best studied reagent in this group of compounds;[3a,4a–c] a much smaller number of examples will be presented for **2** and **4a–c**. While we will show that these low oxidation state transition-metal compounds are catalytically active, interesting differences in rates of cycloaddition and catalyst turnover emerge for **1**, **2**, **3d**, and **4a**, as well as the fact that trace impurities and/or decomposition products can be catalytically active and serve to mask the true organometallic catalysis.

Table I. Diels–Alder Reactions of Cyclopentadiene

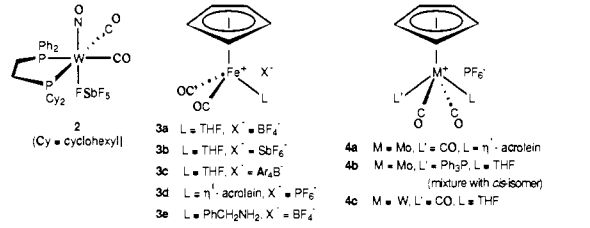
diene	equiv CH_2=C(H)C(O)R	R	catalyst[a]	time[b]	endo:exo	yield, %
1.01	1	H	none	1	80:20	16–35
1061	1049	H	**1**	1	84:16	89
1039	1029	H	**3a**	1	92:8	83
106	101	H	**4c**	3	80:20	76
1.08	1	Me	none	1	88:12	22
106	101	Me	**1**	1	95:5	92
986	975	Me	**3a**	5.6	95:5	78
103	103	Me	**4c**	3	95:5	66[c]
1.04	1	OMe	none	1	87:13	2[d]
106	100	OMe	**1**	1	92:8	85
104	102	OMe	**3a**	24	86:14	17–42[e]
99	112	OMe	**4c**	24	82:18	24[f]

[a] 1 equiv. [b] In hours. [c] Reaction without catalyst for 3 h gave a 62% yield, but the endo:exo ratio was 84:16. [d] Reaction for 24 h gives a 57% yield of product having an endo:exo ratio of 81:19. [e] $CHCl_3$-soluble polycyclopentadiene[1] was also obtained (30% in the experiment where the Diels–Alder yield was 42%, 66% where the Diels–Alder yield was 17%). [f] A 42% yield of $CHCl_3$-soluble polycyclopentadiene[1] was also obtained.

Table II. Diels–Alder Reactions of Butadiene

diene	equiv CH_2=C(H)C(O)R	R	catalyst[a]	time[b]	yield, %
110	100	H	**1**	0.25[c]	100[d]
1130	1000	H	**1**	17[c]	77
39	41	H	**3a**	24[e]	38
44	44	H	**4c**	24	18
1.00	1	Me	none	24	0
120	40	Me	**1**	42[c]	73
40	40	Me	**3a**	24	22
40	42	Me	**3a**	5 days	52
119	47	Me	**4b**	24	15
40	40	Me	**4c**	24	37
60	20	Et	**1**	12[c]	47
60	20	OMe	**1**	20 days	78[d]
60	20	OMe	**1**	13	25[f]
40	41	OMe	**3a**	24	0
39	39	OMe	**4c**	24	0

[a] 1 equiv. [b] In hours. [c] Entire reaction at room temperature. [d] NMR yield. [e] Held at 0 °C for 3.3 h before warming to room temperature. [f] 41 °C.



2 (Cy = cyclohexyl)

3a L = THF, X^- = BF_4^-
3b L = THF, X^- = SbF_6^-
3c L = THF, X^- = Ar_4B^-
3d L = η³-acrolein, X^- = PF_6^-
3e L = $PhCH_2NH_2$, X^- = BF_4^-

4a M = Mo, L' = CO, L = η³-acrolein
4b M = Mo, L' = Ph_3P, L = THF (mixture with *cis*-isomer)
4c M = W, L' = CO, L = THF

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(7) Many Lewis acid induced Diels–Alder reactions require 20–200 mol % of the Lewis acid; see for instance ref 5g–i,m,o, 6a,l–o.

Table III. Diels–Alder Reactions of Isoprene

diene	equiv CH_2=C(H)C(O)R	R	catalyst[a]	time[b]	1,4:1,3	yield, %
1.01	1	H	none	24	69:31	5[c]
106	102	H	**1**	1	93:7	84[d]
101	103	H	**2**	24	87:13	88
100	101	H	**3a**	1	87:13	54
102	101	H	**3a**	24	87:13	86
105	104	H	**3b**	24	89:11	54
124	111	H	**3c**[e]	24	87:13	86
106	102	H	**3d**	24	92:8	43
103	100	H	**3e**	24	71:29	2
100	100	H	**4a**	24	88:12	47
100	99	H	**4c**	24	89:11	68
1.03	1	Me	none	24	72:28	4[f]
109	100	Me	**1**	24	95:5	68[g]
102	103	Me	**3a**	1	96:4	11
110	106	Me	**3a**	24	96:4	61[h]
92	103	Me	**3a**	24	95:5	63[i]
127	110	Me	**3b**	24	91:9	27
112	101	Me	**3e**	24	71:29	1
101	97	Me	**4c**	24	92:8	68
1.13	1	OMe	none	24		0[j]
100	95	OMe	**1**	24	96:4	12[k]
105	100	OMe	**3a**	24		0
100	100	OMe	**4c**	24		0

[a] 1 equiv. [b] In hours. [c] Reaction of a 1.5:1 ratio of neat isoprene–acrolein at 125 °C for 19 h gives an 89% yield of 59:41 1,4 to 1,3 isomers. [d] 98% yield after 24 h. [e] Ar_4B^- is $[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$. [f] Reaction of a 1.5:1 ratio of neat isoprene–methyl vinyl ketone at 125 °C for 15 h gives an 83% yield of 68:32 1,4 to 1,3 isomers. [g] Use of acetic acid free methyl vinyl ketone gave a 75% yield of identical material. [h] Yields vary with different samples of **3a** from 47 to 78%. [i] Benzene solvent. [j] Reaction of a 1.01:1 ratio of neat isoprene–methyl acrylate at 89 °C for 48 h gives a 73% yield of 68:32 1,4 to 1,3 isomers. [k] A 62% yield of soluble polyisoprene was obtained.

Results and Discussion

Transition-Metal Catalysis. The results of reactions of acrolein, methyl vinyl ketone, and methyl acrylate with cyclopentadiene, butadiene, isoprene, and *trans*-1,3-pentadiene (piperylene), both in the presence and absence of catalysts **1–4**, are collected in Tables I–IV. Overall, we have observed induction of Diels–Alder reactions using no more than 1 mol % of each of **1**, **2**, **3a–d**, and **4a–c**. For cyclopentadiene, high yields are obtained in the reactions with acrolein or methyl vinyl ketone even in the presence of as little as 0.1 mol % of **1** and **3a**. For acrolein, enhancement of the endo:exo ratio[5d,f,t,8] is observed only in the presence of **3a**, while enhancements are observed in all cases for methyl vinyl ketone. For methyl acrylate only **1** is clearly catalytically active and enhances the endo:exo ratio; the 24-h yields for **3a** and **4c** are *lower* than those for the thermal reaction, which may be accounted for by competitive polymerization of the diene[1] in the presence of this least basic enone. The results with cyclopentadiene are perhaps the least striking, however, since the thermal reactions proceed in high yield in only a few hours more time than the catalyzed reactions. For butadiene on the other hand the rate enhancement is enormous: as little as 0.1 mol % of **1** allows isolation of a 77% yield of the acrolein adduct after a 17-h reaction time, while essentially no uncatalyzed reaction occurs at room temperature; typical reaction temperatures are ~130–140 °C.[9] Butadiene reactions in the presence of **3a** were found to yield oligomeric products when carried out exclusively at room temperature, but the simple expedient of adding diene to a solution of enone and catalyst held at 0 °C eliminated this problem, so all subsequent reactions were conducted this way. For convenience

Table IV. Diels–Alder Reactions of *trans*-1,3-Pentadiene

diene	equiv CH_2=C(H)C(O)R	R	catalyst[a]	time[b]	*cis*-1,2: *trans*-1,2: *cis*-1,3	yield, %
1.02[d]	1	H	none	24		2[c]
167[d]	103	H	**1**	1	95:3:2	96
101	100	H	**3a**	24	95:2:3	89
117	106	H	**4c**	24	90:7:3	71
1.00[d]	1	Me	none	24		0[e]
162[d]	109	Me	**1**	24	93:5:2	75[f]
95	95	Me	**3a**	24	95:3:2	55
95	99	Me	**4c**	24	94:4:2	62
1.04[d]	1	OMe	none	24		0[g]
165[d]	104	OMe	**1**	24	95:5[h]	9[i]
101	100	OMe	**3a**	24		0
106	100	OMe	**4c**	24		0

[a] 1 equiv. [b] In hours. [c] Reaction of a 1:1 mixture of neat piperylene–acrolein at ~125 °C for 10 h gives an 80% yield of 73:20:7 *cis*-1,2 to *trans*-1,2 to *cis*-1,3 isomers. [d] Mixture of 61.9% *trans*-piperylene and 38.1% *cis*-piperylene (which does not undergo the Diels–Alder rection); equiv of trans isomer is reported. [e] Reaction of a 1:1 mixture of neat piperylene–methyl vinyl ketone at ~125 °C for 6 h gives a 72% yield of 56:25:12:7 *cis*-1,2 to *trans*-1,2 to *cis*-1,3 to *trans*-1,3 isomers. [f] 17% yield in 1 h. [g] Reaction of a 1:1 mixture of neat piperylene–methyl acrylate at ~125 °C for 6 h gives a 73% yield of 44:40:8:8 *cis*-1,2 to *trans*-1,2 to *cis*-1,3 to *trans*-1,3 isomers. [h] Due to the presence of polymer isomer ratios are taken from the MeO region of the ^1H NMR; the ratio is *cis*-1,2 and *cis*-1,3 to *trans*-1,2. [i] An 89% yield of soluble polypiperylene was obtained; in 1 h yields are 0.5% Diels–Alder adduct and 6% polymer.

and access to information on regioselectivity, the most heavily studied reactions were those with isoprene. Here, room temperature reactions with both acrolein and methyl vinyl ketone proceed in only 4–5% yield in 24 h, giving a ~70:30 ratio of 1,4- to 1,3-substituted cyclohexene isomers, and the uncatalyzed methyl acrylate reaction gives no product. However, catalysis by 1 mol % of **1** gives in only 1 h an 85% yield of 93:7 1,4- to 1,3-substituted acrolein adduct and in 24 h a 68% yield of 95:5 1,4- to 1,3-substituted methyl vinyl ketone adduct;[10] with methyl acrylate a 12% yield of 96:4 1,4- to 1,3-substituted adduct was obtained, but this was accompanied by a 62% yield of polyisoprene.[1] Catalysis by **3a** gives comparable yields for acrolein and methyl vinyl ketone in 24 h but gives no methyl acrylate catalysis, while **4a** and **4c** are perhaps slightly less reactive (i.e. 47% of 88:12 1,4/1,3 isomers for acrolein with **4a** in 24 h, 68% of similar material for **4c**, but a 68% yield of methyl vinyl ketone adduct compared to 47–78% for **3a**). The single result for **2** suggests that it is comparable to **3a** in reactivity. Lastly, the piperylene results also demonstrate rate enhancements and stereoselectivities[10] analogous to those seen with isoprene: uncatalyzed reactions give essentially no product in 24 h, while organometallic catalysis of the acrolein and methyl vinyl ketone reactions proceeded in 55–96% yield. Once again **1** is clearly the most reactive, for instance giving in 1 h a 96% yield of the acrolein adduct and in 24 h the only methyl acrylate adduct; however, in this latter case as with isoprene, piperylene is polymerized, here at roughly 10 times the rate of Diels–Alder cycloaddition. In the absence of enone, piperylene is polymerized by **1** to give soluble polyalkenamer in ~80% yield in 24 h.

A central problem in any study of catalysis is that of whether the true catalytic species is derived from the catalyst precursor added to the reaction mixture or is simply an adventitious impurity introduced by an impure reagent or a minor decomposition pathway. Having shown that Diels–Alder catalysis is effected by addition of substoichiometric quantities of **1–4**, we therefore turned our attention toward determining whether or not these carbonyl compounds were the true catalysts.

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(10) For Lewis acid enhancements of regio- and stereoselectivies in isoprene and piperylene cycloadditions, see ref 5d,f,g,o,s and: (a) Lutz, E. F.; Bailey, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 3899–3901. (b) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 1121–1123. (c) Inukai, T.; Kojima, T. *Ibid.* **1967**, *32*, 869–871. (d) Kugatova-Shemyakina, G. P.; Rozhkova, L. I.; Gramenitskaya, V. N.; Andreev, V. M. *J. Org. Chem. USSR* (*Engl. Transl.*) **1970**, *6*, 2459–2463.

Table V. Comparison of Lewis Acidity

Lewis acid[a]	$\Delta\delta$[b]	relative power[c]
BBr_3	1.49	1.00 ± 0.005
$AlCl_3$	1.23	0.82
BF_3	1.17	0.77 ± 0.02
$EtAlCl_2$	1.15	0.77
$TiCl_4$	1.03	0.66 ± 0.03
$Me_3P(CO)_3(NO)W^+$[d]	0.93	0.62
Et_2AlCl	0.91	0.59 ± 0.03
$SnCl_4$	0.87	0.52 ± 0.04
$Cp(CO)_3Mo^+$[e]	0.70	0.47
Et_3Al	0.63	0.44 ± 0.02
$Cp(CO)_2Fe^+$[f]	0.54	0.36
$(P)_2(CO)_2(NO)W^+$[g]	0.28	0.19

[a] B, Al, Ti, and Sn Lewis acids taken from ref 11c. [b] Downfield shift of H3 of crotonaldehyde upon coordination; chemical shift of H3 of free crotonaldehyde in CD_2Cl_2 at 23 °C is δ 6.863. [c] $\Delta\delta$(adduct)/$\Delta\delta$(BBr_3); standard deviations for literature data come from comparisons with several bases. [d] Adduct prepared in situ from **1**. [e] Isolated as PF_6^- salt. [f] Isolated as the BF_4^- salt. [g] Adduct prepared in situ from **2**.

Lewis Acidity. As a simple starting point, the order of catalytic activity, **1** > **2** ≈ **3a** ≥ **4a**, **4c** is expected to correlate with Lewis acidity. A number of acidity scales based on NMR chemical shift differences between free and Lewis acid complexed bases have been described,[11] including one due to Childs[11c] in which coordination of crotonaldehyde gives a downfield shift of the 3-hydrogen in the ^1H NMR. We therefore recorded the ^1H NMR spectra of the crotonaldehyde adducts related to **1**–**4** in order to place them on this Lewis acidity scale; results are listed in Table V along with some of Childs' data. As expected,[5o] $AlCl_3$ is near the top of the list; that it is more reactive than **1** for instance is evident from catalysis of methyl acrylate reactions with isoprene and piperylene by 10 mol % of $AlCl_3$.[10b,c] Where comparative results are available,[5c,g,i,j,o,6p,12] catalytic activity following the order $AlCl_3$ > $EtAlCl_2$ > Et_2AlCl > $TiCl_4$, BF_3 > $SnCl_4$ has been seen, with the order of $TiCl_4$, BF_3, and $SnCl_4$ being most variable and perhaps a function of competing polymerization. The acidity of BBr_3 seems not to correlate with Diels–Alder activity,[5o] while the three aluminum Lewis acids seem to be closer in reactivity than this scale would suggest. Nevertheless, on the basis of this NMR scale **1** is comparable in acidity to $TiCl_4$ and Et_2AlCl, both of which are good Lewis acid Diels–Alder catalysts,[5b,i,j,u,6p,r,12] **4** is comparable to $SnCl_4$[5b–d,g,i,o,6p,v,12] and Et_3Al,[5j] the weakest acids for which data was tabulated, and **3** is obviously weaker yet. We suggest that the NMR result for **2** is anomolous and is due to shielding of the crotonaldehyde methine hydrogen by a phenyl ring of the chelating $Cy_2PCH_2CH_2PPh_2$ ligand. Consistent with this interaction, the phenyl region in the ^1H NMR spectra of both the crotonaldehyde and acrolein adducts is quite different from that of the isoprene–acrolein Diels–Alder and SbF_6^- adducts, where in the latter cases the phenyl resonances overlap from ~7.6 to 7.5 ppm while in the former cases four multiplets are spread out from ~7.67 to 7.35 ppm. The acidity order **1** > **2** > **4a** > **3a** is inherently reasonable, since **2** has a donor $-CH_2Ph_2P$ group in place of a π-acid CO ligand and so is less acidic than **1**, both **4a** and **3a** have donor cyclopentadienyl rings and so are less acidic than **1** and **2**, while **3a** has only two π-acid CO ligands and so is less acidic than **4a**, which has three CO ligands. The surprise, then, is the prediction that **3a** should be a poorer catalyst than **4a**, in sharp contrast to the observed results that **3a** is somewhat *more* reactive than **4a** and in some cases comparable to **1** in activity. Thus, the complete failure of the expected correlation of reactivity with acidity for **3a** raised the serious possibility that catalysis in this case was the result of adventitious impurities.

Trapping of Acidic Impurities. We start by proposing three hypothetical impurities, namely, Ag^+, H^+, and BF_3. The first could come from the $Ag^+BF_4^-$ used in the synthesis of **3a** from $Cp(CO)_2FeI$, the second might come from hydrolysis or solvent decomposition, and the third via abstraction of F^- from BF_4^-, perhaps by $Cp(CO)_2Fe^+$ to give $Cp(CO)_2FeF$. Representative results described in this section are collected in Table VI; full details may be found in the supplementary material.

The catalytic activity of $Ag^+BF_4^-$ was tested first and found to be strikingly similar to **3a**. For instance, $Ag^+BF_4^-$ gives the same high yield and surprisingly high endo to exo enhancement for cyclopentadiene and acrolein as does **3a**, and isoprene and piperylene regio- and stereoselectivities are high and all essentially the same; yields with butadiene are higher for acrolein but lower for methyl vinyl ketone. Many attempts were made to ensure the complete absence of $Ag^+BF_4^-$ in the samples of **3a** used. For instance, excess $Cp(CO)_2FeI$ was used in the synthesis of **3a**, and **3a** was repeatedly washed with THF, in which $Ag^+BF_4^-$ is somewhat soluble while **3a** is insoluble. These strategies failed to eliminate (or even significantly change) the activity of **3a**. If $Ag^+BF_4^-$ were truly the catalyst, it would have to be reactive at very low concentrations since it could only be present in **3a** as a minor impurity. However, reaction of isoprene and methyl vinyl ketone with 0.1 mol % of $Ag^+BF_4^-$, which would imply a 10% impurity in **3a**, gave a significantly reduced yield, and in fact no such level of impurity is present. Reasoning that perhaps the synthesis of **3a** gives some type of "activated" $Ag^+BF_4^-$, we treated a batch of $Ag^+BF_4^-$ exactly as it would be in the preparation of **3a**, but without addition of $Cp(CO)_2FeI$. While the resultant silver salt was somewhat more reactive, it still seemed not to account for the reactivity of **3a**.

Having failed to differentiate between the reactivity of **3a** and $Ag^+BF_4^-$ and having found only suggestive evidence that the silver salt could not be reactive enough to itself be the true catalyst, we sought a compound that might react with Ag^+ but not $Cp(CO)_2Fe^+$, perhaps on the basis of steric bulk. The reagent 2,6-di-*tert*-butylpyridine (**5**) has been used as a bulky base that will only accommodate H^+;[13] in Brown's original paper that described its use,[13a] he showed that it would not, for instance, combine with BF_3, and we have confirmed this in solution by examination of the ^1H NMR of $BF_3{\cdot}Et_2O$ and **5** in CD_2Cl_2. On the basis of ^1H NMR, **5** also does not displace THF from **3a**. Thus, while **5** will react with any adventitious acid and we hoped with any adventitious Ag^+ as well, since it does not react with the iron center of **3a**, it seemed that it could not directly interfere with any catalysis that **3a** might induce.

As we had hoped, addition of at least 1 equiv (relative to the catalyst) of 2,6-di-*tert*-butylpyridine to $Ag^+BF_4^-$ and $H^+BF_4^-$ resulted in complete inhibition of catalysis; only the thermal Diels–Alder reaction was seen. In the $Ag^+BF_4^-$ reaction, a gray precipitate formed, which we assume is the silver–base adduct. Much more important, however, was the discovery that when *less* than 1 equiv of base was added to the $Ag^+BF_4^-$ reaction, the catalytic reaction was *also* completely inhibited, as shown for isoprene with acrolein (where 0.2 equiv of base was used) and for methyl vinyl ketone (where 0.16 and 0.35 equiv of base were used). Thus, *silver cation cannot be a catalyst.*

Results with **3a** proved to be somewhat more ambiguous. For instance, the catalyzed reaction of isoprene with methyl vinyl ketone was *completely inhibited by addition of 0.29 equiv of* ***5*** *relative to* ***3a***. However, reaction of isoprene with acrolein in the presence of 0.31 equiv of base for 1 h gave a 3% yield of Diels–Alder adduct with a 1,4:1,3 ratio of 85:15; since the thermal reaction only proceeds in 5% yield in 24 h and gives an isomer ratio of 69:31, some residual catalytic activity seemed apparent. Reaction in the presence of 0.35 and 0.71 equiv of base gave 26% and 20% yields, respectively, after 24 h (compared to 86% in the absence of base), and the isomer ratios are essentially unchanged as a function of time or presence of base. The lower yield could

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Table VI. Selected Diels–Alder Reactions in the Presence of 2,6-Di-*tert*-butylpyridine (**5**) and Catalysis by Potential Impurities

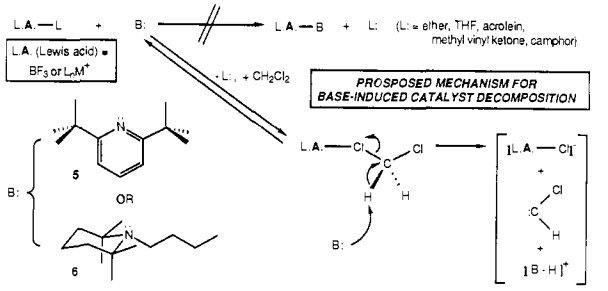
	diene	equiv CH_2=C(H)C(O)R	R	base[a]	catalyst[b]	time[c]	selectivity[d]	yield, %
1029	cyclopentadiene	1026	H		$Ag^+BF_4^-$	1	91:9	73
41	butadiene	42	H		$Ag^+BF_4^-$	24		77
89	isoprene	87	H		$Ag^+BF_4^-$	24	84:16	86[e]
103	isoprene	91	H	0.20	$Ag^+BF_4^-$	24	74:26	5
112	isoprene	111	Me		$Ag^+BF_4^-$	24	96:4	32
947	isoprene	948	Me		$Ag^+BF_4^-$	24	79:21	12
97	isoprene	98	Me	0.16	$Ag^+BF_4^-$	24	76:24	4
94	piperylene	96	H		$Ag^+BF_4^-$	24	95:2:3	89
1008	isoprene	1019	Me		HBF_4·Et_2O	24	95:5	68
102	isoprene	100	Me	0.33	HBF_4·Et_2O	24	96:4	78
102	isoprene	101	Me	2.18	HBF_4·Et_2O	24	77:23	3
105	isoprene	104	H	0.35	**3a**	24	87:13	26
103	isoprene	98	Me	0.29	**3a**	24	78:22	4
92	isoprene	101	H		BF_3·Et_2O	24	88:12	76
101	isoprene	102	H	0.22	BF_3·Et_2O	24	87:13	78
95	isoprene	102	H	1.27	BF_3·Et_2O	24	80:20	53
99	isoprene	100	Me		BF_3·Et_2O	24	95:5	92
95	isoprene	90	Me	0.25	BF_3·Et_2O	24	97:3	74
102	isoprene	100	Me	1.64	BF_3·Et_2O	24	70:30	3
101	isoprene	102	H		$NO^+SbF_6^-$	1	85:15	39
99	isoprene	96	H		$Ph_3C^+PF_6^-$	24	89:11	83
103	isoprene	99	H	0.45	$Ph_3C^+PF_6^-$	24	89:11	52
103	isoprene	101	H	1.57	$Ph_3C^+PF_6^-$	24	68:32	2
186	isoprene	185	Me		$Ph_3C^+PF_6^-$	24	90:10	72
777	isoprene	985	Me		$Ph_3C^+PF_6^-$	24	93:7	65
9410	isoprene	9142	Me		$Ph_3C^+PF_6^-$	24	87:13	19
96	piperylene	95	H		$Ph_3C^+PF_6^-$	24	61:36:3	81
104	piperylene	102	Me		$Ph_3C^+PF_6^-$	24	88:10:2	91

[a] 2,6-Di-*tert*-butylpyridine. [b] 1 equiv. [c] In hours. [d] For cyclopentadiene, endo:exo; for isoprene, 1,4:1,3; for piperylene, *cis*-1,2:*trans*-1,2:*cis*-1,3. [e] 10% of this material is the trioxane.[1]

be due to more efficient scavenging of impurity by base but equally well may be due to experimental error. We suggest that the most likely reason for the difference between the acrolein and methyl vinyl ketone results is simply that acrolein is a more reactive enone in these Diels–Alder reactions, so while cycloaddition of methyl vinyl ketone with isoprene is not catalyzed by **3a** itself, that with acrolein is, giving yields of ~20% after 24 h.

The question of the species scavenged by 2,6-di-*tert*-butylpyridine remains. The obvious choice is H^+ itself,[13] consistent with a control experiment in which addition of less than 1 equiv of base to HBF_4·Et_2O did not inhibit the catalysis. The source of protic acid is not obvious, however. Methylene chloride is well-known to contain traces of acid if not properly purified.[14] However, the uncatalyzed reactions were carried out in a manner exactly analogous to the catalyzed reactions, so there is no acid in the solvent itself that is catalyzing the reaction. Two reactions were conducted in benzene. Reaction of isoprene and methyl vinyl ketone for 24 h in the presence of 1 mol % of **3a** gave a 63% yield of 95:5 1,4:1,3 isomers, while $Ag^+BF_4^-$ gave an 11% yield of 97:3 1,4 to 1,3 isomers, so solvent decomposition is unlikely to be the sole source of catalysis. We next tested BF_3, even though it is supposed to be inert to 2,6-di-*tert*-butylpyridine. Reaction of isoprene and acrolein in the presence of 1 mol % of BF_3·Et_2O gave 76%, 78%, and 53% yields in the presence of 0, 0.22, and 1.27 equiv of base, and methyl vinyl ketone gave 92%, 74%, and 3% yields in the presence of 0, 0.25, and 1.64 equiv of base; in the case giving the 3% yield, the isomer ratio clearly showed the absence of any catalyzed reaction. Surprisingly, then, base did seem to inhibit catalysis by BF_3 despite the absence of any observed stoichiometric interaction with it. Two types of control experiments were then conducted to test the apparently differing degrees of inhibition for the two enones. In the first, since methyl vinyl ketone contains 0.12 mol % of acetic acid as a stabilizer, which in the presence of base might be deprotonated to generate an anion that could deactivate BF_3, the effect of acetic acid was examined. Diels–Alder reactions of BF_3·Et_2O (as well as of **3a**) with excess

Scheme I



base were repeated using acetic acid doped acrolein and acetic acid free methyl vinyl ketone, and the results were found *not* to depend on the presence or absence of acetic acid. In the second set of control experiments, 1:1 mixtures of BF_3·Et_2O and **5** in CD_2Cl_2 in the absence and presence of excess acrolein and methyl vinyl ketone were examined by ^1H NMR. In the absence of enone, as noted above no stoichiometric displacement of ether from BF_3 occurred, but after 25 min 3% of the base apparently had been *protonated*, as judged by the appearance of a new *tert*-butyl peak identical with that of independently prepared $[\mathbf{5}\cdot H]^+BF_4^-$. When 14 equiv of acrolein was added to a freshly prepared solution of BF_3·Et_2O and **5**, *26%* of the base was apparently protonated within 25 min, while when 10 equiv of acetic acid free methyl vinyl ketone was used, *58%* of the base was apparently protonated within 25 min. As shown in Scheme I, we propose that *Lewis acid coordination of methylene chloride leads to solvent deprotonation by the hindered base with concomitant catalyst destruction via formation of* BF_3Cl^-. Methyl vinyl ketone apparently promotes this catalyst deactivation reaction more rapidly than does acrolein, which could be a contributing factor in the greater inhibition by base of the methyl vinyl ketone reactions catalyzed by BF_3 and **3a**. Nevertheless, since the amount of free BF_3 in (for instance) $Ag^+BF_4^-$ would be very low, substoichiometric amounts of **5** relative to $Ag^+BF_4^-$ would yield a huge excess of **5** relative to BF_3, and so could halt any catalysis by this impurity for both enones.

Since a role for BF_3 seemed possible in the catalytic activity of **3a**, several analogues were tested (Table III). Since formation

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of SbF_5 via cleavage of an Sb–F bond would be much less likely than B–F cleavage to give BF_3,[15] the SbF_6^- analogue **3b** and $Ag^+SbF_6^-$ were each examined. The former was active although the yield was lower and only suffered a small further decrease in the presence of 0.28 equiv of 2,6-di-*tert*-butylpyridine, consistent with true catalysis by $Cp(CO)_2Fe^+$, while the latter was comparable to $Ag^+BF_4^-$, consistent only with a common impurity or coincidence. The next analogue, **3c**, makes use of the Ar_4B^- counterion, which cannot generate a sufficiently reactive Lewis acid catalyst upon Ar^- abstraction. We initially prepared $Cp(CO)_2Fe(THF)^+Ph_4B^-$, and as hoped this is *not* a catalyst, on the basis of NMR experiments. However, the iron center is slowly phenylated (a known reaction of the Ph_4B^- ion[16]), so one could argue that catalysis by $Cp(CO)_2Fe^+$ is slow and this is a deactivation route. In order to generate a more clear-cut result, the more stable borate ion $[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ was used.[17] In this case, $Cp(CO)_2Fe(THF)^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ is stable to arylation, and the compound seems more stable than **3a** in solution as judged by reduced precipitation on standing. However, **3c** is surprisingly *more* reactive than **3a** in the presence of base, in the isoprene–acrolein reaction. This was examined further by NMR. Addition of excess acrolein to **3c** yields the acrolein adduct by displacement of THF, but further addition of isoprene leads to immediate cycloaddition of the *free* acrolein; only after it is used up is any coordinated Diels–Alder adduct observed, and since additional acrolein does not instantly displace the adduct, the only conclusion is that catalysis is due to unobserved impurities and not **3c**. While the cause is unknown, **3c** is made by metathesis of **3a** and so the same impurity could have been unintentionally concentrated. The isolable PF_6^- acrolein adduct **3d** gives a lower yield than **3a** for the isoprene–acrolein cycloaddition, and the yield drops in half (to 22%) upon addition of 0.19 equiv of base. In order to be sure that the iron cation was having *some* effect, **3e** was examined, with the expectation that the benzylamine ligand would be too tightly bound to dissociate and so no reaction was anticipated; in this case at least our prediction was correct. In conclusion, all that is clear is that the $Cp(CO)_2Fe^+$ ion is not itself the catalyst responsible for the high reactivities seen in Tables I–IV. It is possible that it gives rise to low cycloaddition yields in the isoprene–acrolein reactions, on the order of 15–20% when one subtracts out the thermal reaction. The nature of the catalytic impurity is unknown, but since it seems most closely associated with the BF_4^- ion, BF_3 or some reaction product derived from it with solvent or iron seems most likely.

Having cast doubt on the role of **3a** in catalysis by the use of hindered base **5**, it was obviously necessary to similarly examine the other catalysts. On the basis of the ^{31}P NMR, the SbF_6^- ligand of **1** is not displaced by **5**,[18] but slow formation of protonated base is observed, accounting for 14% of the base in 40 min. However, when **5** was added to acrolein adduct **1a**, *immediate* formation of protonated base was observed along with simultaneous consumption of the tungsten center to give uncharacterized decomposition products: none of the acrolein and little of the Me_3P ligand could be accounted for in the ^1H and ^{31}P NMR spectra. Like **1a**, the acrolein adduct **4a** also was immediately decomposed by addition of **5**, yielding an insoluble precipitate. While it is reasonable to invoke the same decomposition route described above for BF_3 in Scheme I, it occurred to us that alkylation of the aromatic nucleus of 2,6-di-*tert*-butylpyridine,[13a] perhaps by acrolein under the influence of the tungsten species followed by destruction of some intermediate tungsten–oxo species, could be an unnecessary complication. The nonaromatic hindered base tetramethylpiperidine (TMP) was therefore tried, and it led to immediate decomposition of *both* **1** and **1a**. However, models were inconclusive on the question of coordination, and since TMP is a secondary amine rather than tertiary, we examined one last hindered base, 1-(*n*-butyl)-2,2,6,6-tetramethylpiperidine[19] (**6**). While the reaction of **6** with **1** (like that of **5**) was slow, immediate destruction of acrolein adduct **1a** was again observed, and identical results were obtained with methyl vinyl ketone and camphor adducts of **1** that were prepared in situ (Scheme I). These results prompted us to recheck **3a**. It in fact leads to *slow* protonation of **5** and immediately decomposes in the presence of both TMP and **6**, while the isolated acrolein adduct $Cp(CO)_2Fe(\eta^1\text{-}OHCCH{=}CH_2)^+BF_4^-$ was found to decompose faster in the presence of **5** than did THF adduct **3a**. This result could account for the lower yield mentioned above for acrolein adduct **3d** in the presence of **5** rather than the decrease being due to scavenging by **5** of a catalytic impurity. We conclude that, just as seen in the reactions of $BF_3{\cdot}Et_2O$ with **5**, the methylene chloride solvent is not innocent but rather is deprotonated by **5** and **6**, and as shown in Scheme I the source of the intractable decomposition in the transition-metal Lewis acid reactions is the proposed formation of chlorocarbene. Both protonated bases are readily observed in all of the above decomposition reactions, although no effort was made to examine the ^2H NMR from the CD_2Cl_2 reactions since the signal from the acid proton in each of independently prepared $\mathbf{5}{\cdot}H^+BF_4^-$ and $\mathbf{6}{\cdot}H^+BF_4^-$ was quite broad. We suggest that the stronger transition-metal Lewis acids **1a** and **4a** readily coordinate methylene chloride and activate it toward deprotonation, while the weaker acid **3a** only induces this reaction in the presence of the stronger base **6** ($pK_a \approx 11$–12 compared to **5**, $pK_a \approx 5$).[20] The fact that **1** only leads to slow solvent deprotonation suggests that acrolein as well as methyl vinyl ketone or camphor plays a kinetic role[21] in coordination of the solvent, and of course exactly the same kinetic effect is seen in the reactions of $BF_3{\cdot}Et_2O$ and **3a**, where the enones are proposed to enhance ether and THF displacement by methylene chloride. While these results represent in small degree a digression from the main topic here, the potential use of noncoordinating bases as a *test* for methylene chloride coordination via observation of deprotonation is unprecedented and will be the subject of further study. A related observation has been made by Gladysz, where coordination of methylene chloride was proposed to activate it toward S_N2 attack by BF_4^-, generating BF_3, CH_2ClF, and Cl^-.[22] This could of course provide an alternative mechanism for generation of BF_3 in **3a** and $Ag^+BF_4^-$ but would not account for their activity in benzene.

While the use of **5** or **6** was rendered meaningless in terms of trapping potential impurities in reactions of **1** and **4a**, testing of the cationic reagents used in their syntheses was still important. For **1**, $NO^+SbF_6^-$ was tested as a catalyst for reaction of isoprene with acrolein and methyl vinyl ketone; the relatively low yields (39% for acrolein in 1 h and 37% for methyl vinyl ketone in 24 h compared to 85% and 68%, respectively, for **1**) suggest that it

(15) We are aware of only one example of Sb–F cleavage in SbF_6^- (ref 15a), while fluoride cleavage in BF_4^- and PF_6^- is relatively common; see for example: (a) Marks, T. J.; Seyam, A. M. *Inorg. Chem.* **1974**, *13*, 1624–1627. (b) Snow, M. R.; Wimmer, F. L. *Aust. J. Chem.* **1976**, *29*, 2349–2361. (c) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740–5748. (d) Velthuizen, W. C.; Haasnoot, J. G.; Kinneging, A. J.; Rietmeijer, F. J.; Reedijk, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1366–1368. (e) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 7302–7306. (f) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082–1084. (g) Raab, K.; Beck, W. *Chem. Ber.* **1985**, *118*, 3830–3848. (h) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718–1719. (i) Connor, J. A.; James, E. J.; Overton, C.; Walshe, J. M. A.; Head, R. A. *J. Chem. Soc., Dalton Trans.* **1986**, 511–515. (j) Ellis, R.; Henderson, R. A.; Hills, A.; Hughes, D. L. *J. Organomet. Chem.* **1987**, *333*, C6–C10.

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(20) (a) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5444–5447. (b) Hibbert, F.; Awwal, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 939–945. (c) McDaniel, D. H.; Özcan, M. *J. Org. Chem.* **1968**, *33*, 1922–1923.

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(22) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207–219.

Note added in proof: Structural characterization of a compound that exhibits methylene chloride coordination to Ag^+ has recently been reported: Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762–3764.

Table VII. Rate Constants[a] for Cycloaddition and Aldehyde Exchange from Stoichiometric Reactions

compd	k_1, M^{-1} s^{-1}	k_2 or k'_2[b]	k_3 or k'_3[b]	k_4/k_5	k_{dec}, s^{-1}	k_{cyclo}, s^{-1}	$k_{turnover}$, s^{-1}
1a	7.75×10^{-1}	3.20×10^{-1} M^{-1} s^{-1}	1.43×10^{-1} M^{-1} s^{-1}		0	3.9×10^{-1}	1.6×10^{-1}
2	2.25×10^{-1}	2.58×10^{-3} M^{-1} s^{-1}	1.90×10^{-3} M^{-1} s^{-1}		0	1.1×10^{-1}	1.3×10^{-3}
3d	1.14×10^{-2}	1.88×10^{-3} s^{-1}	4.23×10^{-4} s^{-1}	1.91×10^{-1}	5.67×10^{-5}	5.7×10^{-3}	1.6×10^{-3}
4a	8.95×10^{-2}	3.49×10^{-3} s^{-1}	6.42×10^{-4} s^{-1}	2.09×10^{-1}	4.35×10^{-4}	4.5×10^{-2}	2.9×10^{-3}

[a] Rate constants defined in Scheme II and eq 2–4, where for k_{cyclo} and $k_{turnover}$ the concentrations [isoprene], [acrolein], and [Diels–Alder adduct] are taken to be 0.5 M. Reaction temperatures are the following: **1**, 10 °C; **2**, 12 °C; **3d**, 18 °C; **4a**, 10 °C. [b] k_2 and k_3, M^{-1} s^{-1}. k'_2 and k'_3, s^{-1}.

is not involved. For **4a–4c**, $Ph_3C^+PF_6^-$ was tested. With two exceptions, none of the results were inconsistent with catalysis by Ph_3C^+ as an impurity, in terms of regio- and stereoselectivity. With piperylene, however, the cis:trans ratios of the 1,2 isomers dropped from 13 to 1.7 for acrolein and from 24 to 9 for methyl vinyl ketone, for **4c** and $Ph_3C^+PF_6^-$, respectively. The dependence of yield on concentration of $Ph_3C^+PF_6^-$ was examined for isoprene and methyl vinyl ketone, giving yields of 72%, 65%, and 19% using 0.5, 0.13, and 0.01 mol %, respectively, of catalyst. Such a result would again require a ~10% impurity of $Ph_3C^+PF_6^-$ to give the observed yields, and since this is not the case we again conclude that the transition-metal catalysis is real. Last, we note that, unlike the case with $Ag^+BF_4^-$, trityl cation catalysis of the isoprene–acrolein reaction is quenched only by addition of excess **5**.

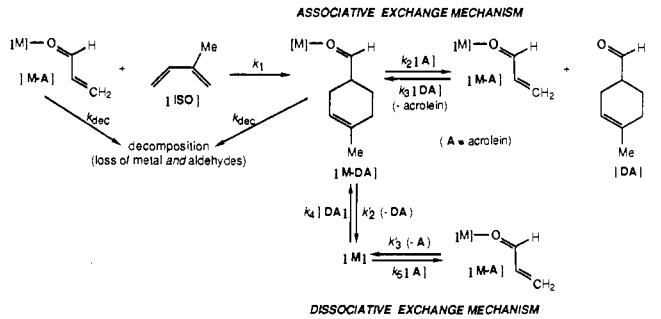
Stoichiometric Reactions and Kinetics. The above results clearly show that one or more impurities apparently present in **3a** are catalytically active, but a small residual activity that accounts for ~20% yields—consistent with the Lewis acidity established by the NMR scale in Table V—is also apparent. While it is impossible to absolutely rule out, there is no clear evidence that any of the results with **1**, **2**, and **4** are due to impurities. Nevertheless, the effects are modest by comparison to other Lewis acids, and the presumption might be that the relatively low *activity* of **1–4** is due to the relatively low *acidity* of these compounds, since this would account for the modest enhancements of rate and stereoselectivity. Such a presumption ignores the *catalytic* nature of the reaction, however. That is, a reagent such as $AlCl_3$ binds aldehydes and ketones so tightly that it typically *must* be present in stoichiometric[7] quantities[5g,o,8b] since dissociation of the Diels–Alder adduct may not occur,[5o] although weaker coordination of less basic esters does allow use of substoichiometric quantities.[5c,i,u,8a,10b,c] In true catalysis, the rate of product dissociation, that is, turnover, will also affect the observed catalytic reactivity. One would expect high acidity to be associated with a rapid rate of Diels–Alder cycloaddition but with a slow rate of turnover. That is, in the truly *catalytic* reaction, these factors *oppose* each other, so the overall rate as a function of acidity would appear to be unpredictable. We therefore undertook a kinetic study of the reactions of **1–4** in order to determine the relative rates of these steps as well as to confirm the identity of the active catalysts as the transition-metal cations.

The qualitative results are readily described. It was found that the acrolein but not the methyl vinyl ketone adducts of the transition-metal cations were crystalline, so this enone was used in all stoichiometric reactions; isoprene was used as the diene in order to prove via the regiochemistry that the catalyzed reaction was indeed being observed. For **1**, cycloaddition was found to be complete within ~1–2 min, both at room temperature and at 10 °C, giving the bound Diels–Alder adducts in a ~90:10 ratio as judged by ^1H NMR.[23] Addition of 3 equiv of acetonitrile to displace the adducts, followed by isolation and purification, gives material identical with the catalytic product. In a separate experiment, further addition of acrolein to the bound Diels–Alder adducts results in complete equilibration, within ~1 min as well, of coordinated acrolein and Diels–Alder adduct; the equilibrium constant for eq 1 is 2.5 ± 0.2 at 10 °C. The cycloaddition for

$$[L_nM\text{-(Diels–Alder adduct)}]^+ + \text{acrolein} \rightleftarrows [L_nM\text{-(acrolein)}]^+ + \text{Diels–Alder adduct} \quad (1)$$

(23) Integration of the peaks due to the coordinated adducts gives less precise ratios than does that of the peaks in the free adducts since the chemical shifts are too close (see the Experimental Section for details).

Scheme II



2 is slower, being ~98% complete in 4 min at room temperature and ~60% complete in 1 min at 12 °C; the 1,4:1,3 isomer ratio of the bound adduct is readily determined by ^1H NMR to be 89:11, which compares with 87:13 for the catalytic reaction. Equilibration is much slower, however, requiring more than 1 h. For **3a**, cycloaddition is much slower, requiring over 1 h for completion, but the isomer ratio of 87:13 is obviously consistent with Lewis acid catalysis and is identical with that seen in the *catalytic* reaction of **3a** in the presence of **5**. Addition of acrolein apparently results in slow equilibration as well. Since catalyst decomposition, which also removes aldehyde from solution, occurs at a rate comparable to approach to equilibrium, the time to reach the endpoint could not be determined; even after 1.5 h, however, the ratio of acrolein adduct to Diels–Alder adduct was still changing. For **4a**, both the cycloaddition and turnover rates are intermediate: the initial reaction takes ~20 min, while equilibration is apparently slow, but like the iron case competitive decomposition precludes quantitative determination of the equilibrium point. This qualitative description allows us to conclude that *counter to expectation, the rates of cycloaddition and aldehyde exchange do not have to oppose each other: the strongest acid yields the faster rates for each, and the weakest acid, the slowest rates for each.* Since such a result was so unexpected, we sought greater precision in the description of these rates.

In order to measure rate constants, an explicit reaction mechanism must be proposed. Two are shown in Scheme II. Common points are the presumed bimolecular cycloaddition step and the presumed unimolecular decomposition of both the acrolein and Diels–Alder adducts. This rate takes into account the observed loss of both aldehydes and organometallic compounds relative to an internal standard; no attempt was made to distinguish the two rates of decomposition from each other, if indeed they are different. The two mechanisms differ in the aldehyde exchange step, which may be associative or dissociative. The latter mechanism will yield via the steady-state approximation an additional variable, namely the ratio of fast rate constants for trapping of the unsaturated metal fragment by either aldehyde, k_4/k_5. While data for the equilibration portion of these stoichiometric reactions was collected for two different concentrations of acrolein in an attempt to help distinguish the mechanisms, only in the case of **2** was the data sufficiently reliable to be helpful; for **1a** the exchanges were done by the first NMR time point, while for **3d** and **4a** the amount of decomposition in these runs was too great. For each catalyst, rate constants were fit to the observed time point data using a computer program[24] that numerically integrates the rate equations and

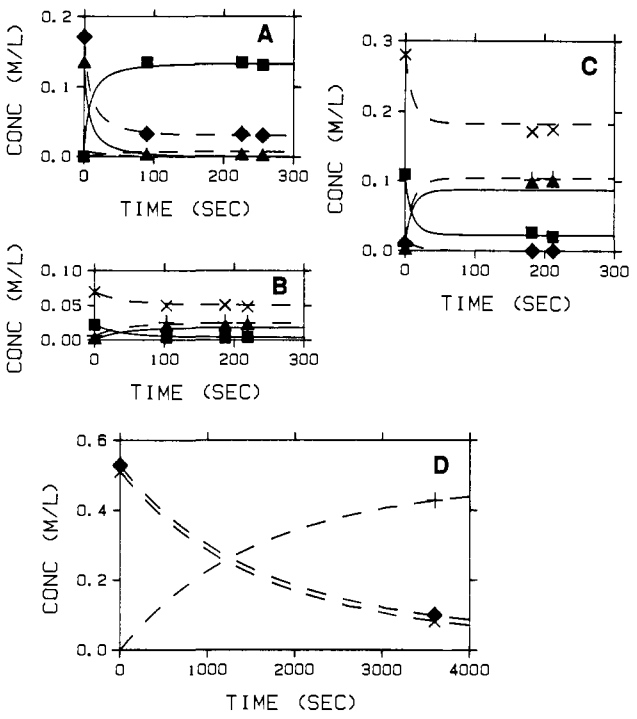


Figure 1. Observed time-point data and calculated concentrations using rate constants in Table VII for **1a**. Observed data: ▲, bound acrolein; ■, bound Diels–Alder adduct; ◆, isoprene; ×, free acrolein; +, free Diels–Alder adduct. Calculated concentrations: solid lines, metal complexes; dashed lines, free organics. Note that (a)–(c) are plotted at the same concentration scale, while (d) is smaller by a factor of 2. (a) Stoichiometric cycloaddition of isoprene. (b) Low concentration exchange of acrolein and bound Diels–Alder adduct. (c) High concentration exchange of acrolein and bound Diels–Alder adduct. (d) Catalytic experiment giving 84% yield in 1 h; metal compounds (at 1 mol %) not shown.

iteratively fits the calculated concentrations to all of the data simultaneously by a method of steepest descent in order to give the best fit rate constants. Since for **1** only minimum rates were directly available since the stoichiometric reactions were done by the time of the first observation, the result from the 1 h catalytic reaction (giving an 84% yield) was also input as a data point for comparison.

The results, collected in Table VII and illustrated in Figures 1–4, demonstrate the validity of the qualitative conclusions above. The cycloaddition rate constants k_1 are reliably determined, given the good fit to the observed data for the reactions of metal–acrolein adducts with isoprene in Figures 2–4; for **1a** in Figure 1, the rate constant is as noted above a lower limit only. Quantitatively, the ratio of relative magnitudes of rate constants[25] of cycloaddition for **1a**, **2**, **4a**, and **3d** is 68:20:8:1, demonstrating that **3d** is substantially less reactive than any of the other catalysts, given the nearly order of magnitude difference in rate constants between **3d** and **4a**, and **4a** is similarly less reactive than **1a**. As anticipated, these rates are directly correlated with the apparent Lewis acidity of the cations. The rate constants for turnover are much more difficult to quantitatively establish. In the best case, that of **2**, the best fit is obtained using the associative mechanism, a result that is especially believable since it requires one less variable than the dissociative mechanism. For this reason we have also fit the data for **1a** to the associative mechanism, and in fact both associative and dissociative ligand substitution is known in tungsten chemistry.[26] Both **3d** and **4a** give acceptable *overall* fits to the associative mechanism, but the critical data points arise from the free acrolein that is present and subsequently displaces the bound Diels–Alder adduct; the fit for the free aldehydes is good in both cases only for the dissociative mechanism. In order to directly compare the various cycloaddition and turnover rates, pseudo-first-order rate constants are defined in eq 2–4 and listed in Table VII; for simplicity the conversion of the acrolein adduct back to the Diels–Alder adduct is ignored. In this way, the cycloaddition rates k_{cyclo} are seen to range from ~2 to ~16 times greater than the turnover rates for **1a**, **3d**, and **4a**, and ~87 times greater for **2**, therefore both justifying the above simplification and demonstrating that *turnover is the rate-determining step in the catalytic reactions*. This is seen most dramatically in Figure 2, where cycloaddition results in consumption of the acrolein adduct within the first few minutes of reaction time, but then due to the presence of excess acrolein the concentration of the acrolein adduct slowly builds back up. We propose that the relative rates of turnover may be accounted for by π-back-bonding. The weakest acid, **3d**, also should be the best π-donor, and donation of electron density into the enone or Diels–Alder adduct carbonyl π^*-orbital should serve to enhance the metal–oxygen bond strength; evidence that π-back-bonding can occur in **3a** comes from the many well-known $Cp(CO)_2Fe(\eta^2\text{-olefin})^+$ complexes, which require this interaction for stability.[4a-c] On the other hand, we have *never* observed olefin coordination to **1**, suggesting that π-back-bonding in the coordination site trans to the strong π-acid nitrosyl ligand is not possible. The turnover rate for **4a** is slightly faster (by a factor of 2) than that for **3d**, so one might conclude that these slow rates will be typical of cyclopentadienyl compounds, while the turnover rate for **2** is actually *slower*. This effect could be due to steric inhibition of associative exchange by the bulky chelating ligand, rather than due to π-back-bonding.

$$\frac{-d[L_nM\text{-(acrolein)}^+]}{dt} = k_1[\text{isoprene}][L_nM\text{-(acrolein)}^+] = k_{cyclo}[L_nM\text{-(acrolein)}^+] \quad (2)$$

$$\frac{d[L_nM\text{-(acrolein)}^+]}{dt} = k_2[\text{acrolein}][L_nM\text{-(DA adduct)}^+] = k_{turnover}[L_nM\text{-(DA adduct)}^+] \quad (3)$$

$$\frac{d[L_nM\text{-(acrolein)}^+]}{dt} = k'_2\left(\frac{[\text{acrolein}]}{(k_4/k_5)[\text{DA adduct}] + [\text{acrolein}]}\right) \times [L_nM\text{-(DA adduct)}^+] = k_{turnover}[L_nM\text{-(DA adduct)}^+] \quad (4)$$

The rates measured in stoichiometric reactions can now be used to predict product yields under catalytic conditions.[24] For **1**, the 1-h catalytic data point was used to refine the rate constants and allows the prediction that the reaction would be complete within ~6 h, consistent with the observed result. For **2**, the integrated rate equations predict the reaction will be 80% complete in 24 h, consistent with the observed 88% yield in 24 h; given the ~10 °C temperature difference between the stoichiometric and catalytic reactions, the agreement is remarkable. For **3a**, the prediction is that the reaction with isoprene and acrolein will proceed in only 7% yield in 24 h, and due to catalyst decomposition the reaction will be done at that point, in reasonable agreement with our prediction of 15–20% yields made on the basis of reactions in the presence of **5**. For **4a**, the prediction is that the reaction will only proceed to ~1% completion, due to catalyst decomposition. Since both **3a** and **4a** are proposed to undergo dissociative aldehyde exchange, it is possible that each undergoes faster decomposition

(24) CRK (for *C*omplex *R*eaction *K*inetics program), W. H. Hersh. Required input includes differential equations for all non-steady-state reaction species, observed concentration vs time points, and initial guesses for each rate constant; numerical integration is accomplished by a fourth-order Runge–Kutta method. Estimated yields for the catalytic reactions are then obtained by numerical integration of the same equations using the derived best fit rate constants, with the further input only of the initial concentrations of the organic reactants and catalyst. Data are plotted using a program written by G. A. Merry, 1985.

(25) These values ignore the effect of reaction temperature; kinetics with **1**, **2**, and **4a** were carried out at 10–12 °C and so are directly comparable, while **3d** was examined at 18 °C and so the rates will appear *faster* than they should.

(26) (a) Angelici, R. J. *Organomet. Chem. Rev.* **1968**, *3*, 173–226. (b) Dobson, G. R. *Acc. Chem. Res.* **1976**, *9*, 300–306.

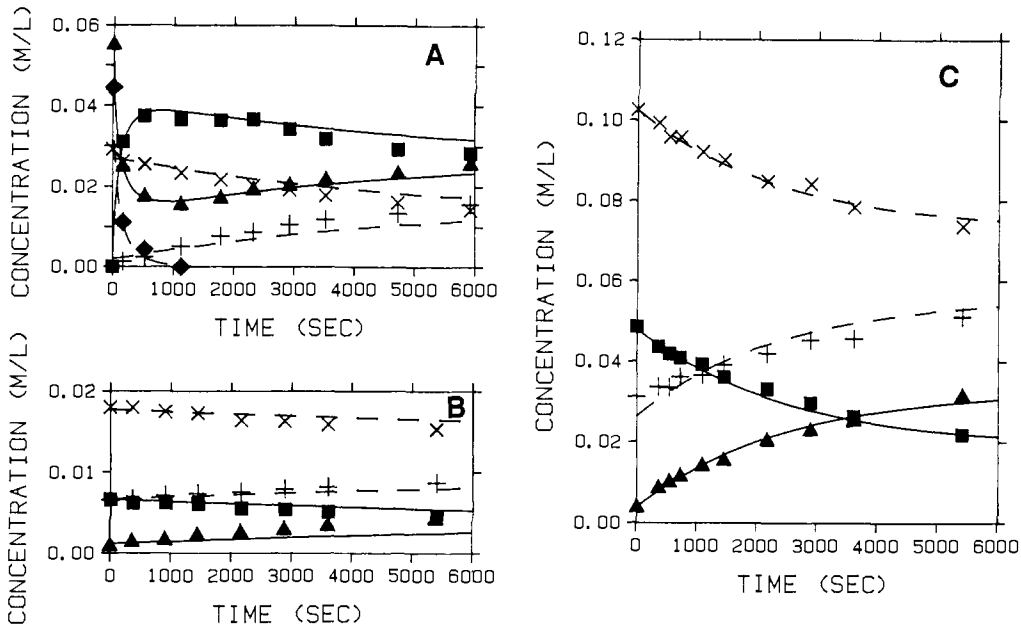


Figure 2. Observed time-point data and calculated concentrations using rate constants in Table VII for acrolein adduct of **2**. For readability about half of the data points before 1000 s are not plotted. See Figure 1 for key. Note that (a) and (c) are plotted at the same concentration scale, while (b) is expanded by a factor of 2. (a) Stoichiometric cycloaddition of isoprene. (b) Low concentration exchange of acrolein and bound Diels–Alder adduct. (c) High concentration exchange of acrolein and bound Diels–Alder adduct.

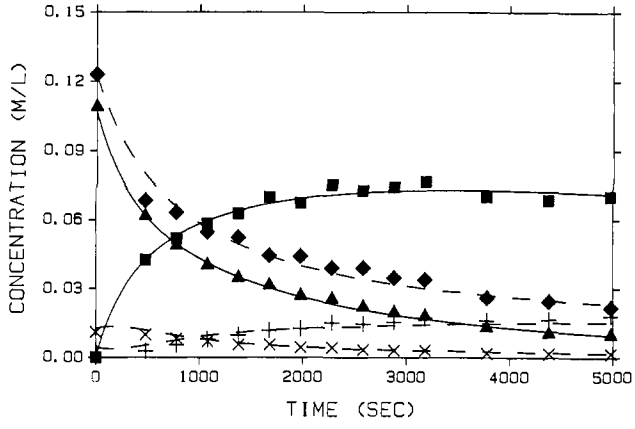


Figure 3. Observed time-point data and calculated concentrations using rate constants in Table VII for cycloaddition reaction of isoprene with **3d**. See Figure 1 for key.

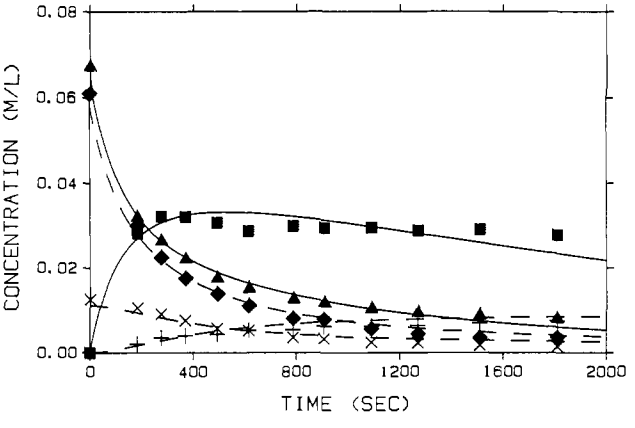


Figure 4. Observed time-point data and calculated concentrations using rate constants in Table VII for cycloaddition reaction of isoprene with **4a**. For readability about half of the data points before 800 s are not plotted. See Figure 1 for key.

at low aldehyde concentration due to slower trapping of the 16-electron intermediate. Thus, under catalytic conditions decomposition might be mitigated. However, when the course of the reaction is recalculated using a 10-fold slower decomposition rate (comparable to that seen with **3a**), the yield only increases to 14%, but since the rate-limiting step is only twice as fast as that of **3a**, this is the expected result. Since the temperature for the stoichiometric reaction of **4a** was ~10 °C lower than in the catalytic reaction, it is still possible that **4a** is the true catalyst, but we cannot rule out catalysis by impurities. Thus, both **3a** and **4a** are catalysts but both are slow, and unfortunately **3a** (and possibly **4a** as well) is always contaminated by a much better catalyst whose exact identity is unknown, although BF_3 and H^+ remain as candidates. The only comparable rate data of which we are aware is due to Inukai and Kojima, who measured $AlCl_3$-catalyzed cycloaddition of isoprene and methyl acrylate;[10b,27] at room temperature, $k_1 \approx 1 \times 10^{-2}$ M^{-1} s^{-1}, and cycloaddition, not turnover, was found to be rate-limiting. The rate constant is actually the same as that for **3a** albeit with the much more reactive dienophile acrolein, but the comparison nevertheless makes clear that the low reactivity of **3a** is a function of slow turnover and not slow cycloaddition.

Conclusion

The kinetic results finally provide definitive evidence that the organometallic cations derived from **1**, **2**, **3a**, and **4a** are true Diels–Alder catalysts; the *stoichiometric* rates and observed *catalytic* yields are in complete agreement for **1** and **2**, while for **3a** and **4a** the true catalysis by $Cp(CO)_2Fe^+$ and $Cp(CO)_3Mo^+$ is much slower than that observed. We have shown that the rates of cycloaddition follow the order **1** > **2** > **4a** > **3d** and are directly correlated with the Lewis acidity of the cations. Surprisingly, the rates of turnover, aside from the anomolously slow exchange in sterically hindered **2**, are also loosely correlated with the Lewis acidity of the cations, which we suggest is accounted for by increased π-back-bonding to the enone with decreasing acidity. At some point of increasing acidity the enone to metal donor bond would presumably lead to a decrease in rate of turnover, but that point has not been detected yet in the cation series we have examined; in principle, however, it could fall between **1** and **2**. Nonetheless, the surprising and clear result of the kinetic analysis is that it is the rate of turnover and not that of cycloaddition that is in need of enhancement in order to give a better catalyst.

In conclusion, we have shown that low oxidation state transition-metal cations can be true Lewis acid Diels–Alder catalysts.

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More importantly, we have demonstrated that observation of such catalysis does not constitute proof that the presumed catalyst is the active species. The use of reagents that can trap impurities but leave the transition-metal species untouched is appealing but in this case proves to be useful only for the weakest Lewis acids, specifically Ag^+ and $Cp(CO)_2Fe^+$. For the more acidic tungsten nitrosyl reagents, we have shown that kinetic analysis of stoichiometric rates of cycloaddition and turnover can predict overall reaction rates of the catalytic reactions and so constitutes the best available evidence of the identity of the catalytic species. Indeed, Halpern has pointed out that in the absence of such kinetic evidence the simple observation of a species in a catalytic cycle cannot constitute proof of its involvement,[28] and in fact for $Cp(CO)_3Mo^+$ such kinetic evidence is lacking. Since these organometallic catalysts are not terribly reactive, their utility lies in the potential for design of asymmetric analogues. Cyclopentadienyl analogues of **4a** and **3a** are clearly not reactive enough to pursue as initial targets, while steric hindrance in **2** may be an insurmountable problem in rate enhancement. The clear-cut result is that the best choice will be a close analogue of the tungsten nitrosyl compound **1**. In the final analysis, the best evidence that these materials are the true catalysts will be the demonstration that a chiral analogue is capable of induction of asymmetric Diels–Alder reactions, and work in that direction is in progress.

Experimental Section

All manipulations of air-sensitive compounds were carried out either in a Vacuum Atmospheres inert atmosphere glovebox under recirculating nitrogen or by use of standard Schlenk techniques. NMR spectra were recorded on IBM AF-200 and Bruker WP-200, AM-360, and AM-500 spectrometers; chemical shifts are reported relative to TMS in $CDCl_3$, residual $CHDCl_2$ (^1H, δ 5.32) in CD_2Cl_2 (^{13}C, 53.8 ppm), C_6HD_5 (^1H, δ 7.15) in C_6D_6 (^{13}C, 128.0 ppm), 8.5% H_3PO_4 in a 1-mm coaxial tube (^{31}P, 0.00 ppm), and internal $Me_3PW(CO)_5$ (^{31}P, −38.03 ppm in CD_2Cl_2). Infrared spectra were obtained in CH_2Cl_2 in 0.1-mm NaCl solution cells on a Perkin-Elmer 237 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Desert Analytics, Tucson, AZ. Mass spectra (EI) were obtained on an AEI MS902.

All solvents were treated under nitrogen. Tetrahydrofuran, benzene, and ether were distilled from sodium benzophenone ketyl, methylene chloride was distilled from phosphorus pentoxide, methylene chloride-d_2 was vacuum-transferred from phosphorus pentoxide, and hexane was washed successively with 5% nitric acid in sulfuric acid, water, and saturated aqueous sodium carbonate and then distilled from *n*-butyllithium. Benzylamine (MCB), crotonaldehyde (MCB), 2,6-di-*tert*-butylpyridine (**5**; Aldrich), cyclopentadiene (cracked from the dimer, Eastman Kodak), and all other Diels–Alder reactants (Aldrich) were purified by vacuum-transfer from CaH_2, with the exception of butadiene (Union Carbide, Matheson, and Aldrich), which was transferred from a gas cylinder attached to a vacuum line to give a 1.0 M solution in methylene chloride; each reactant was then stored at −40 °C. Except as noted in Table III and in the supplementary material, enones were stabilized as follows: acrolein, 0.10 wt % of hydroquinone; methyl vinyl ketone, 0.1 wt % of acetic acid, 0.05 wt % of hydroquinone; methyl acrylate, 0.02 wt % of hydroquinone. Phosphines ($Ph_2PC(H)=CH_2$ and $(C_6H_{11})_2PH$; Aldrich), silver salts and $NO^+SbF_6^-$ (Ozark-Mahoning), and $HBF_4\cdot Et_2O$ (Aldrich) were used as received, while $BF_3\cdot Et_2O$ (Alfa) was purified by vacuum transfer. Compounds **1**,[2] **1a**,[1,2b] **3a**,[29] **4b**,[4d,e] and **4c**[4d,e] were prepared according to published procedures. All of the cationic complexes were thermally sensitive and required storage at −40 °C; we presume that it is for this reason that all samples submitted for elemental analysis gave poor results.

***mer*-(*cis*-Me_3P)(*trans*-NO)$(CO)_3W(CH_3CH=CHCHO)^+SbF_6^-$.** About 2 equiv of crotonaldehyde was added to a CD_2Cl_2 solution of **1**: ^1H NMR (adduct only, CD_2Cl_2) δ 9.025 (d, J = 8.79 Hz, *H1*), 7.789 (dq, J = 15.21, 6.95 Hz, 1 H, *H3*), 6.308 (ddq, J = 15.2, 8.8, 1.4 Hz, 1 H, *H2*), 2.252 (dd, $^3J_{HH}$ = 6.95 Hz, $^4J_{HH}$ = 1.38 Hz, 3 H), 1.783 (d, $^2J_{PH}$ = 9.18 Hz, 9 H, PMe_3).

$Cy_2PCH_2CH_2PPh_2$. The chelating ligand was prepared in a manner analogous to a published procedure for $Ph_2PCH_2CH_2PPh_2$.[30] All of the following operations (including chromatography) were carried out under nitrogen. A solution of 5.02 g (23.7 mmol) of $Ph_2PC(H)=CH_2$ in 25 mL of THF was added to a solution of 4.70 g (23.7 mmol) of $(C_6H_{11})_2PH$ and 0.276 g (2.37 mmol) of *p*-tolyllithium in 100 mL of THF, and the mixture was heated at reflux for 16 h. The THF was stripped to give a red oil, which was filtered through a 1-cm pad of silica gel, eluting with 100 mL of ether, to give after solvent removal 5.97 g (68% yield) of product as a yellow oil. This was chromatographed on an 11 × 4 cm silica column, first eluting with 200 mL of hexane and 200 mL of 95:5 hexane–ether and then collecting a fraction in 150 mL of 95:5 hexane–ether that yielded 3.76 g of white powder. This material crystallized over 3 days at −40 °C from 4:1 hexane–methylene chloride and after washing with cold hexane gave 3.23 g of large white crystals: ^1H NMR δ 7.5 (m, 4 H), 7.4–7.1 (m, 6 H), 2.38 (m, 2 H, PCH_2), 1.85–1.45 (m, 14 H, PCH_2 and PCy_2), 1.19 (m, 10 H, PCy_2); ^{31}P NMR (C_6D_6) δ 0.72 (d, $^3J_{PP}$ = 29.7 Hz, Ph_2P), −12.49 (d, $^3J_{PP}$ = 29.7 Hz, Cy_2P).

$(Cy_2PCH_2CH_2PPh_2)(CO)_2(NO)WBr$. A solution of 3.14 g (~5.7 mmol) of *trans*-$(NO)(CO)_4WBr$ (prepared according to a published procedure[31] that gives material contaminated by ~26% by weight of $W(CO)_6$ on the basis of elemental analysis) and 2.01 g (4.9 mmol) of $Cy_2PCH_2CH_2PPh_2$ in 200 mL of THF was heated at reflux for 40 min to give, after removal of solvent and $W(CO)_6$ by warming under vacuum, 3.66 g (98% yield) of crude product. This was chromatographed ~1 g at a time on a 12 × 2.5 cm silica column with 3:1 benzene–hexane, yielding after a 50-mL forerun a 100-mL fraction that contained pure product as a yellow solid in ~75% yield: IR (benzene) 2017 (s), 1939 (m), 1617 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 7.66–7.57 (m, 4 H), 7.09–7.02 (m, 4 H), 6.99–6.95 (m, 2 H), 2.44 (m, 2 H, PCH_2), 2.25 (m, 2 H, PCH_2), 1.9–0.8 (m, 22 H, $(C_6H_{11})_2P$); ^{13}C NMR (C_6D_6) δ 211.40 (dd, $^2J_{CP(cis)}$ = 6.1 Hz, $^2J_{CP(trans)}$ = 48.9 Hz, *C*O), 209.72 (dd, $^2J_{CP(cis)}$ = 6.5 Hz, $^2J_{CP(trans)}$ = 46.4 Hz, *C*O); ^{31}P NMR (C_6D_6) δ 37.42 (d, J_{PP} = 1.43 Hz, $^1J_{PW}$ = 243.0 Hz, Cy_2P), 32.11 (d, J_{PP} = 1.43 Hz, $^1J_{PW}$ = 246.9 Hz, Ph_2P). Anal. Calcd for $C_{28}H_{36}BrNO_3P_2W$: C, 44.23; H, 4.77; N, 1.84. Found: C, 44.90; H, 4.89; N, 1.79.

$(Cy_2PCH_2CH_2PPh_2)(CO)_2(NO)W(\mu\text{-}F)SbF_5$ (2). Samples were prepared in situ by rapid stirring of (typically) 75 mg (0.099 mmol) of the above bromide in 1 mL of CD_2Cl_2 with 31.3 mg (0.091 mmol, 0.92 equiv) of $Ag^+SbF_6^-$ for 1.5 h and then filtering through a pipet column of oven-dried Celite: ^1H NMR (CD_2Cl_2) δ 7.60–7.49 (m, 10 H), 2.64–2.50 (m, 2 H, PCH_2), 2.3–1.25 (m, 24 H, PCH_2 and $(C_6H_{11})_2P$); ^{31}P NMR (CD_2Cl_2) δ 54.79 (d of sept, J_{PP} = 3.3 Hz, $^2J_{PF}$ = 29.5 Hz, $^1J_{PW}$ = 264 Hz, Cy_2P), 46.71 (d of sept, J_{PP} = 3.4 Hz, $^2J_{PF}$ = 33.0 Hz, $^1J_{PW}$ = 265 Hz, Ph_2P).

$(Cy_2PCH_2CH_2PPh_2)(CO)_2(NO)WL^+SbF_6^-$. Generation of the adducts L = acrolein and crotonaldehyde occurs immediately upon addition of 1–2 equiv of L to **2** in CD_2Cl_2; L = 1-carboxyaldehyde-3 and 4-methyl-3-cyclohexene is prepared by addition of 1 equiv of isoprene to the acrolein adduct: ^1H NMR (CD_2Cl_2) L = acrolein, δ 8.369 (d, J = 8.58 Hz, 1 H), 7.67–7.35 (m, 10 H), 6.821 (d, J = 9.99 Hz, 1 H), 6.467 (d, J = 17.06 Hz, 1 H), 5.874 (m, 1 H), 3.10 (m, 1 H, PC*H*), 2.49 (m, 1 H, PC*H*), 2.37–1.13 (m, 24 H, PCH_2 and $(C_6H_{11})_2P$); L = crotonaldehyde, δ 8.208 (d, J = 8.76 Hz, 1 H), 7.65–7.38 (m, 10 H), 7.139 (dq, J = 15.21, 6.97 Hz, 1 H, *H3*), 5.683 (ddq, J = 15.3, 8.8, 1.4 Hz, 1 H, *H2*), 3.04 (m, 1 H, PC*H*), 2.40 (m, 2 H, PCH_2), 2.3–1.1 (m, 23 H, PC*H* and $(C_6H_{11})_2P$), 2.069 (dd, $^3J_{HH}$ = 6.93 Hz, $^4J_{HH}$ = 1.16 Hz, 3 H); L = 1-carboxaldehyde-3 and 4-methyl-3-cyclohexene, δ 8.79 (d, J = 11.9 Hz, 1 H, 1,3 isomer), 8.77 (d, J = 11.4 Hz, 1 H, 1,4 isomer), 7.62–7.45 (m, 10 H), 5.210 (br d, J = 18.8 Hz, 1 H) 3.20 (m, 1 H, PC*H*), 2.63 (m, 1 H, PC*H*), 1.592 (s, ring methyl), 2.46–0.93 (m, 34 H, PCH_2, $(C_6H_{11})_2P$, and ring hydrogens).

$Cp(CO)_2Fe(THF)^+SbF_6^-$ (3b). This compound was prepared exactly analogously to **3a**:[29] ^1H NMR (CD_2Cl_2) δ 5.37 (s, 5 H, Cp), 3.45 (AA′BB′, 4 H, OCH_2), 1.84 (AA′BB′, 4 H, CH_2); for comparison, chemical shifts for **3a** are δ 5.42, 3.48, and 1.84.

$Cp(CO)_2Fe(THF)^+Ar_4B^-$ (3c). These compounds were prepared by metathesis of **3a** with $Na^+Ph_4B^-$ and $Na^+[3,5\text{-}(CF_3)C_6H_3]_4B^-$[17] as follows: (1) A solution of 0.51 g (1.518 mmol) of **3a** in 3 mL of methylene chloride was added to a solution of 0.53 g (1.549 mmol) of $Na^+Ph_4B^-$ in a mixture of 12 mL of methylene chloride and 2 mL of THF. After the solution was shaken and allowed to stand, a precipitate settled out and was filtered to give 0.36 g of a bright red microcrystalline product, which was recrystallized from methylene chloride/THF and then acetone/ether to give 0.30 g (35% yield): IR (CH_2Cl_2) 2069 (m), 2025 (m) cm^{-1}; ^1H NMR (acetone-d_6) δ 6.31–6.24 (m, 8 H), 5.97–5.91 (m, 8 H), 5.85–5.82 (m, 4 H), 4.89 (s, 5 H, Cp), 3.30, 1.83 (THF, AA′BB′ m). (2) A solution of 195 mg (0.220 mmol) of $Na^+[3,5\text{-}(CF_3)C_6H_3]_4B^-$ (which had been dried under high vacuum for several days to give a brown powder) and 67 mg (0.199 mmol) of **3a** in 1 mL of CH_2Cl_2 was stirred

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for 15 min and then filtered through Celite. After addition of 1 mL of CH_2Cl_2, 2 mL of hexanes was carefully layered on and the mixture allowed to stand for 3 days at −40 °C, giving after filtration and washing with hexanes 145 mg (0.130 mmol, 66% yield) of **3c** as large chunky deep red crystals: IR (CH_2Cl_2) 2070 (vs), 2023 (vs) cm^{-1}; ^1H NMR (CH_2Cl_2) δ 7.73 (br s, 8 H), 7.58 (s, 4 H), 5.23 (s, 5 H, Cp), 3.36, 1.78 (THF, AA′BB′ m); ^{13}C NMR (CD_2Cl_2) δ 208.24 (FeCO), 162.09 (1:1:1:1 q, $^1J_{C^{11}B}$ = 49.8 Hz, *C1*), 135.14 (br s, *C2*), 129.21 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *C3*), 124.94 (q, $^1J_{CF}$ = 272.3 Hz, *C*F_3), 117.86, (sept, $^3J_{CF}$ = 4.0 Hz, *C4*), 85.15 (s, Cp), 82.43 (s, O*C*H_2, THF), 26.55 (s, *C*H_2, THF). Anal. Calcd for $C_{43}H_{25}O_3BF_{24}Fe$: C, 46.43; H, 2.27; F, 40.99. Found: C, 44.58; H, 2.21; F, 37.46.

Cp(CO)$_2$Fe(H$_2$C=CHCHO)$^+$PF$_6^-$ (3d). A mixture of 1.213 g (3.99 mmol) of Cp(CO)$_2$FeI,[32] 1.004 g (3.97 mmol) of $Ag^+PF_6^-$, and 2.256 g (40.24 mmol) of acrolein in 20 mL of CH_2Cl_2 was stirred for 2 h. The solvent was removed and the residue extracted with 40 mL of CH_2Cl_2 and filtered through Celite. The filtrate was concentrated to ~20 mL, and 30 mL of ether was layered on. After standing at −40 °C for 22 h, 839 mg (2.22 mmol, 56% yield) of **3d** as dark red crystals was obtained upon filtration and washing with ether: ^1H NMR (CD_2Cl_2) δ 9.13 (d, J = 8.4 Hz, 1 H), 6.76 (d, J = 10.1 Hz), 6.69 (d, J = 17.2 Hz, 1 H), 6.40 (m, 1 H), 5.38 (s, 5 H, Cp).

Cp(CO)$_2$Fe(PhCH$_2$NH$_2$)$^+$BF$_4^-$ (3e). A solution of benzylamine (0.25 mL, 2.3 mmol) and **3a** (310 mg, 0.92 mmol) in 5 mL of CH_2Cl_2 was stirred for 10 min; the color changed from deep red to yellow-amber within the first few seconds. The solvent volume was concentrated to about 2 mL, and 10 mL of ethyl ether was added with cooling to precipitate the product as a yellow solid (230 mg, 67% yield). This material was recrystallized once from CH_2Cl_2–ether for use in the catalytic reactions: IR (CH_2Cl_2) 2046 (vs), 2001 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.36–7.29 (m, 5 H), 5.20 (s, 5 H, Cp), 3.418, 3.396 (AB q, J_{AB} = 6.2 Hz, 2 H, CH_2), 3.17 (br s, 2 H, NH_2).

Cp(CO)$_2$Fe(CH$_3$CH=CHCHO)$^+$BF$_4^-$. A solution of crotonaldehyde (270 mg, 3.85 mmol) and **3a** (65 mg, 0.19 mmol) in 1 mL of CH_2Cl_2 was stirred for 1 h. The solvent was evaporated, the resultant red oil taken up in 1 mL of CH_2Cl_2, and 3 mL of ethyl ether layered on. After standing at −40 °C for 4 h, the red material, which precipitated as a gum, was again extracted with CH_2Cl_2, the solvent evaporated, and the residue triturated with ether. The solid that formed was dried to give 30 mg (47% yield) of the crotonaldehyde adduct: ^1H NMR (CD_2Cl_2) δ 9.047 (d, J = 8.54 Hz, 1 H), 7.403 (dq, J = 15.13, 7 Hz, 1 H, *H3*), 6.179 (dd, J = 15.14, 8.53 Hz, 1 H, *H2*), 5.373 (s, 5 H, Cp), 2.092 (d, J = 7 Hz, 3 H).

Cp(CO)$_3$Mo(H$_2$C=CHCHO)$^+$PF$_6^-$ (4a). The procedure is based on that for **4b** and **4c**,[4d,e] and modified to help ensure the absence of $Ph_3C^+PF_6^-$ in the product. Solid CpMo(CO)$_3$H (0.819 g, 3.33 mmol) was added to a −40 °C solution of $Ph_3C^+PF_6^-$ (1.20 g, 3.09 mmol) in 20 mL of CH_2Cl_2. The solution of Cp(CO)$_3$Mo$^+PF_6^-$ was divided in half and a solution of 198 mg of acrolein (3.53 mmol) in 1 mL of CH_2Cl_2 added to one portion. After filtration through Celite and standing at −40 °C overnight, the solution was filtered to give after washing first with cold CH_2Cl_2 and then with hexane 270 mg (39% yield) of **4a** as purple crystals: ^1H NMR (CD_2Cl_2) δ 9.21 (d, J = 8.5 Hz, 1 H), 6.96 (d, J = 10.3 Hz, 1 H), 6.87 (d, J = 17.3 Hz, 1 H), 6.51 (m, 1 H), 6.01 (s, 5 H, Cp). Anal. Calcd for $C_{11}H_9O_4PF_6Mo$: C, 29.62; H, 2.03; F, 25.55. Found: C, 27.93; H, 2.04; F, 22.39.

Cp(CO)$_3$Mo(CH$_3$CH=CHCHO)$^+$PF$_6^-$. To the remaining portion of Cp(CO)$_3$Mo$^+PF_6^-$ prepared as described for **4a** was added a solution of crotonaldehyde (244 mg, 3.48 mmol) in 1 mL of CH_2Cl_2, and the solution was filtered as above. No crystals formed on standing at −40 °C, so an equal volume of hexane was layered on, yielding after cooling overnight and washing with hexane 497 mg (70% yield) of product as purple-red crystals: ^1H NMR (CD_2Cl_2) δ 9.036 (d, J = 8.68 Hz, 1 H), 7.566 (dq, J = 15.29, 6.95 Hz, 1 H, *H3*), 6.300 (ddq, J = 15.37, 8.67, 1.45 Hz, 1 H, *H2*), 5.99 (s, 5 H, Cp), 2.202 (dd, $^3J_{HH}$ = 6.97 Hz, $^4J_{HH}$ = 1.39 Hz, 3 H).

1-(*n*-Butyl)-2,2,6,6-tetramethylpiperidine (6). While this compound has been mentioned in the literature,[19c] no procedure or data are available; the following is based on procedures for related compounds.[19a,b] A mixture of 3.90 g (27.6 mmol) of tetramethylpiperidine, 26.86 g (146 mmol) of *n*-butyl iodide, and 5.51 g (40 mmol) of K_2CO_3 in 30 mL of dimethylformamide was heated under nitrogen at ~50 °C for 37 h. After addition of 50 mL of ~2 M NH_4OH, the mixture was extracted with benzene, and the organic phase was dried over K_2CO_3, stripped, and subjected to fractional distillation. A forerun consisting of solvent and reactants was discarded, and a 3.49-g fraction (64% yield) of nearly pure **6** (containing minor amounts of DMF and an unidentified impurity) distilling at 145–154 °C (52 mmHg) was collected. This was redistilled to give a 1.09-g fraction, bp 115–6 °C (25 mmHg), of 6 that was deoxygenated by three freeze–pump–thaw cycles, stored over sieves under nitrogen, and used for all further experiments: ^1H NMR (C_6D_6) δ 2.35 (m, 2 H, NCH_2), 1.54–1.43 (m, 4 H, NCH$_2$CH_2 and C(4)H_2), 1.40–1.37 (m, 4 H, C(3,5)H_2), 1.21 (sext, J = 10.4 Hz, 2 H, CH_2CH$_3$), 1.19 (s, 12 H, Me$_4$), 0.92 (t, 3 H, J = 10.2 Hz, CH$_2$CH_3); ^{13}C NMR (C_6D_6) δ 54.51 (s, C2, C6), 45.12 (t, C1′), 41.59 (t, C3, C5), 38.68 (t, C2′), 27.70 (br q, Me$_4$), 20.98, 18.22 (t, C3′, C4), 14.43 (q, C4′); MS (70 eV) *m/e* 197 (M^+, 25%), 182 ($M^+ - CH_3$, 100%), 154 ($M^+ - C_3H_7$, 68%). Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.02; H, 14.13; N, 6.76.

Diels–Alder Reactions. All reactions were carried out in the same way, except as noted in the tables and in the supplementary material. In a typical procedure, 21.3 mg (0.0349 mmol) of **1** and 200 mg (3.57 mmol) of acrolein were combined in 4 mL of methylene chloride in a 25-mL flask, which was fitted with a septum-capped pressure-equalizing addition funnel to which had been added 251.7 mg (3.70 mmol) of isoprene in 3 mL of methylene chloride. The apparatus was then removed from the glovebox, the solution cooled to 0 °C, and the diene added dropwise over ~1–2 min. The reaction was stirred an additional 10 min at this temperature, and then the ice bath was replaced by a room temperature water bath; the addition funnel was replaced by a ground-glass stopper. After 1 h, the solution was filtered through 10 mL of silica in 10 mL of methylene chloride on a frit in order to remove catalyst, and the product was washed through with a further 15–25 mL of methylene chloride. Solvent removal on a rotary evaporator yielded 381.4 mg (86%) of product as a colorless liquid; analysis by ^1H NMR indicated the presence of 2.5% by weight of methylene chloride, giving a final yield of 84%.

Compounds were identified by NMR comparison to authentic material made as described in the literature.[8,10,33] Isomer ratios were determined by ^1H NMR ($CDCl_3$) integration of the enone aldehydic or methyl hydrogen atoms of the cyclopentadiene adducts, the aldehydic hydrogen atoms of the acrolein–isoprene adducts, and ring methyls of the remaining isoprene and piperylene adducts (with use made of the acrylate methoxy resonances when the ring methyls were obscured by polymers) as follows: cyclopentadiene–acrolein (endo) δ 9.419 (d, $^2J_{HH}$ = 2.8 Hz), (exo) δ 9.795 (d, $^2J_{HH}$ = 2.4 Hz); cyclopentadiene–methyl vinyl ketone (endo) δ 2.134, (exo) δ 2.218; cyclopentadiene–methyl acrylate (endo) δ 3.627, (exo) δ 3.693; isoprene–acrolein (1,4) δ 9.687 (d, J = 1.7 Hz), (1,3) δ 9.695 (d, J = 1.2 Hz); isoprene–methyl vinyl ketone (1,4) δ 1.651, (1,3) δ 1.678; isoprene–methyl acrylate (1,4) δ 1.647, 3.679, (1,3) δ 1.667, 3.688; piperylene–acrolein (*cis*-1,2) δ 0.991 (d, J = 7.2 Hz), 9.788 (d, J = 1.2 Hz), (*trans*-1,2) δ 1.052 (d, J = 7.0 Hz), 9.685 (d, J = 2.2 Hz, overlaps *cis*-1,3), (*cis*-1,3) δ 1.033 (d, J = 7.1 Hz); piperylene–methyl vinyl ketone, (*cis*-1,2) δ 0.839 (d, J = 6.9 Hz, (*trans*-1,2) δ 0.936 (d, J = 7.0 Hz), (*cis*-1,3) δ 1.011 (d, J = 6.9 Hz), (*trans*-1,3) δ 1.025 (d, J = 6.8 Hz); piperylene–methyl acrylate, (*cis*-1,2) δ 0.893 (d, J = 7.0 Hz), 3.690 (overlaps 1,3), (*trans*-1,2) δ 0.986 (d, J = 7.0 Hz), 3.699, (*cis*-1,3) δ 1.001 (d, J = 7.1 Hz), 3.688 (*cis*- or *trans*-1,3), (*trans*-1,3) δ 1.012 (d, J = 7.1 Hz).

Polymerization of Piperylene. In a manner exactly analogous to the above Diels–Alder reactions, a mixture of 0.368 g (5.41 mmol) of 61.9% *trans*-piperylene and 38.1% *cis*-piperylene in 3 mL of methylene chloride was added to 19.9 mg (0.033 mmol) of **1** in 4 mL of methylene chloride at 0 °C and after 10 min placed in a room temperature water bath and stirred for 24 h. The clear yellow solution was filtered through 10 mL of silica gel in 10 mL of methylene chloride and further eluted with an additional 15 mL of solvent. Solvent removal on a rotary evaporator gave 0.296 g (80% yield) of a noncrystalline white solid, which on the basis of comparisons to literature NMR data[34] consists of 15–35% *trans*-1,2-polypentadiene and 65–85% *trans*-1,4-polypentadiene. *trans*-1,2-Polypentadiene: ^1H NMR ($CDCl_3$) δ 5.13 (br m, 1 H), 4.95 (br m, 1 H), 1.92 (br, CH; overlaps 1,4 isomer), 1.639 (d, J = 4.0 Hz, CH$_3$), 1.20 (br, CH$_2$); ^{13}C NMR ($CDCl_3$) δ 135.66, 122.65, 40.34 (*C*H$_2$; overlaps 1,4 isomer), 36.92 or 36.64 (*C*H), 17.98 (*C*H$_3$). *trans*-1,4-Polypentadiene: ^1H NMR ($CDCl_3$) δ 5.31 (br, 2 H), 2.0 (m, CH and CH$_2$), 0.937 (d, J = 6.4 Hz, CH$_3$); ^{13}C NMR ($CDCl_3$) δ 137.30, 126.60, 40.34 (*C*H$_2$; overlaps 1,2 isomer), 36.92 or 36.64 (*C*H), 20.06 (*C*H$_3$).

Kinetics. All reactions were followed by ^1H NMR (500 MHz) in a temperature-controlled probe; temperatures are listed in Table VII. For **1a**, **3d**, and **4a** 1,2,4,5-tetrachlorobenzene was used as an internal integration standard (δ 7.59, CD_2Cl_2), while for **2** (MeO)$_3$PW(CO)$_5$ (δ 3.64,

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(34) (a) Beebe, D. H.; Gordon, C. E.; Thudium, R. N.; Throckmorton, M. C.; Hanlon, T. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2285–2301. (b) Aubert, P.; Sledz, J.; Schuē, F.; Brevard, C. *Ibid.* **1981**, *19*, 955–972.

d, J = 11.8 Hz, CD_2Cl_2) was used. In all cases, the acrolein adduct and integration standard were dissolved in CD_2Cl_2 and transferred to an oven-dried 5-mm NMR tube in the glovebox, and the tube was capped with a rubber septum and further sealed with Parafilm. The height (h, in centimeters) of the solution in the tube was used to compute the volume (milliliters) using the formula $V = \pi(0.213)^2h$. A "zero-point" spectrum was then recorded 2–5 min prior to injection of isoprene; decomposition during this time was negligible. The initial isoprene concentration was estimated by extrapolation from the sum of the observed quantities of isoprene and Diels–Alder adducts (both free and bound) in the first few spectra taken. After completion of the cycloaddition (consumption of isoprene) and equilibration (no further change in free and bound acrolein and Diels–Alder adduct concentrations), the samples were returned to the glovebox. Precipitates were filtered through Celite on a wad of glass wool in a pipet (all oven dried) from the **3d** and **4a** reactions, and a small aliquot (about one-third to one-fifth of the total volume) was transferred to a second NMR tube. After recording the solution height additional solvent was added to this latter tube to give the desired concentration. Each NMR tube was then capped as before and a zero-point spectrum recorded for both the original undiluted sample ("concentrated") and the second "dilute" sample. Acrolein was then added by syringe to each sample to initiate the turnover reaction; while 1.4–5 equiv was used, for each metal a similar number of equivalents was used for both the concentrated and dilute samples, thereby allowing the concentrations but not the relative amounts to differ significantly. Rather than using the measured amount of acrolein (see below) to determine the initial concentration, a zero-point estimate was made by extrapolation from the sum of the observed quantities of free and bound acrolein in the first few spectra taken and subtraction of the amount of bound acrolein in the zero-point spectrum. The concentrations of free and bound acrolein, free and bound Diels–Alder adducts, and isoprene were obtained by comparison of the integrated peak intensities of the aldehydic and (for isoprene) olefinic resonances to that of the internal integration standard, the concentration of which was known. For the associative mechanism (Scheme II) the data was fit to eq 5–9, and for the dissociative mechanism, to eq 9–13,

$$d[M\text{–}A]/dt = -k_1[M\text{–}A][\text{isoprene}] + k_2[A][M\text{–}DA] - k_3[DA][M\text{–}A] - k_{dec}[M\text{–}A] \quad (5)$$

$$d[M\text{–}DA]/dt = k_1[M\text{–}A][\text{isoprene}] - k_2[A][M\text{–}DA] + k_3[DA][M\text{–}A] - k_{dec}[M\text{–}DA] \quad (6)$$

$$d[A]/dt = -k_2[A][M\text{–}DA] + k_3[DA][M\text{–}A] \quad (7)$$

$$d[DA]/dt = k_2[A][M\text{–}DA] - k_3[DA][M\text{–}A] \quad (8)$$

$$d[\text{isoprene}]/dt = -k_1[M\text{–}A][\text{isoprene}] \quad (9)$$

$$d[M\text{–}A]/dt = -k_1[M\text{–}A][\text{isoprene}] + R_1[A] - k'_3[M\text{–}A] - k_{dec}[M\text{–}A] \quad (10)$$

$$d[M\text{–}DA]/dt = k_1[M\text{–}A][\text{isoprene}] - k'_2[M\text{–}DA] + R_2[DA] - k_{dec}[M\text{–}A] \quad (11)$$

$$d[A]/dt = -R_1[A] + k'_3[M\text{–}A] \quad (12)$$

$$d[DA]/dt = k'_2[M\text{–}DA] - R_2[DA] \quad (13)$$

where

$$R_1 = \frac{k'_2[M\text{–}DA] + k'_3[M\text{–}A]}{(k_4/k_5)[DA] + [A]}, \quad R_2 = \frac{k'_2[M\text{–}DA] + k'_3[M\text{–}A]}{[DA] + (k_5/k_4)[A]}$$

the concentrations of free and bound acrolein and free and bound Diels–Alder adducts are indicated by [A], [M–A], [DA], and [M–DA], respectively.

For **1a**, 48.3 mg (0.0725 mmol) and 14.5 mg (0.0672 mmol) of $C_6H_2Cl_4$ were used; since the reaction was fast the NMR tube was cooled to −78 °C prior to addition of 7 μL (~0.07 mmol) of isoprene. For the turnover reactions, the concentrations of all species in the concentrated and dilute samples differed by a factor of 4.56 prior to acrolein addition at 0 °C; 7.4 μL (0.111 mmol) of acrolein was added to the concentrated sample and 2.8 μL (0.042 mmol) to the dilute sample.

The acrolein adduct of **2** was prepared in situ as described above, by addition of 7.0 μL (0.105 mmol) of acrolein to 0.046 mmol of **2** in CD_2Cl_2; 16.6 mg (0.037 mmol) of $(MeO)_3PW(CO)_5$ was used. Isoprene (5 μL, ~0.05 mmol) was added at room temperature, and after 2 h an additional 2 μL of isoprene was added to consume the remaining acrolein. For the turnover reactions, the concentrations of all species in the concentrated and dilute samples differed by a factor of 5.73 prior to acrolein addition at room temperature; 4.1 μL (0.061 mmol) of acrolein was added to the concentrated sample and 1.0 μL (0.015 mmol) to the dilute sample.

For **3d**, 43.5 mg (0.115 mmol) was used but was first dissolved in CD_2Cl_2 and filtered into 25.5 mg (0.118 mmol) of $C_6H_2Cl_4$; 11 μL (~0.11 mmol) of isoprene was added at room temperature. For the turnover reactions, the concentrations of all species in the concentrated and dilute samples differed by a factor of 2.08 prior to acrolein addition at room temperature; 8.0 μL (0.120 mmol) of acrolein was added to the concentrated sample and 8.0 μL (0.120 mmol) to the dilute sample. While a slow but steady drop in total concentration of all aldehydes was observed in the cycloaddition reaction—that is, metal decomposition resulted in aldehyde loss rather than in release of free aldehyde—in both turnover reactions free acrolein concentration dropped sharply during the first 20 min to about half its initial concentration without any concomitant increase in bound acrolein or free Diels–Alder adduct. After that point all concentrations changed slowly but the data was not used to calculate rate constants due to the unexplained behavior of the reaction. At the end of the concentrated reaction a weighed amount of ferrocene was added to recalculate the concentration of the internal standard, and it was found to be completely unchanged from the cycloaddition reaction.

For **4a**, 21.0 mg (0.047 mmol) and 10.4 mg (0.048 mmol) of $C_6H_2Cl_4$ were used; 4.8 μL (~0.048 mmol) of isoprene was added at room temperature. For the turnover reactions, the concentrations of all species in the concentrated and dilute samples differed by a factor of 3.08 prior to acrolein addition at room temperature; 8.1 μL (0.121 mmol) of acrolein was added to the concentrated sample and 3.8 μL (0.057 mmol) to the dilute sample. As in the case of **3d**, a steady decrease in aldehyde concentration was observed in the cycloaddition reaction, while in the turnover experiments the concentration of acrolein decreased steadily over the first 15 min of reaction time to about two-thirds the initial concentrations but again without any concomitant changes in bound acrolein or free Diels–Alder adduct; the data were not used for rate constant calculations.

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Supplementary Material Available: Table of 65 Diels–Alder reactions catalyzed by potential impurities and/or carried out in the presence of **5** (2 pages). Ordering information is given on any current masthead page.