change depends upon the quantity of Cs^+ present. The value of $r_{C=C}$ increases from 1.34 ± 0.01 Å for ethylene on the Ag catalyst with no added Cs^+ to 1.39 ± 0.01 Å for ethylene on 30% Cs^+/Ag catalyst. It is apparent that the double bond in ethylene has become weaker due to an interaction of the Cs^+ with the silver and/or the ethylene. Again, Carter and Goddard[4] have argued that Cs^+ should facilitate the binding of ethylene to the surface.

There are at least two explanations[8] for the observed changes of the chemical shift and bond length. First, it is known that electron density can be transferred from the alkali to the transition metal.[9] By such a transfer, silver is expected to become enriched in valence electron density, thereby altering its interaction with ethylene and facilitating a partial transfer of electron density to the π^* orbital of ethylene. As a result, the C=C bond distance lengthens and the carbons are more shielded, i.e., more like sp^3 carbons. Second, Cs^+ could be associated with the silver and the ethylene via oxygen bridges, as proposed by Carter and Goddard.[4] One can rationalize our data by a variety of hand-waving arguments. However, more experiments are necessary before one can make a clear choice. The results of selective cross-polarization and/or heteronuclear SEDOR[10] experiments will be discussed in a more detailed report on this system. It is believed that this experimental result will be helpful for the development of a model for the role of Cs^+ in the alkali-promoted partial oxidation of ethylene to ethylene oxide via supported Ag catalysts.

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Registry No. C_2H_6, 74-85-1; Cs^+, 7440-46-2; Ag, 7440-22-4.

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(8) A potential problem with these measurements is that the relative orientations of the dipole and shielding tensors could be changing as a function of the Cs^+ added to the surface. The line shape is relatively insensitive to small changes, i.e., ±4°, in these angles. However, if the relative orientations changed by more that ±8°, then one could not extract the bond distances from the line shapes. This possibility would require a strong (direct) interaction between the Cs^+ and the ethylene. The relatively small changes in the observed shielding tensor argue against this as a viable possibility. Hence, we feel that the relative orientations of the two tensors are independent (within the context of small angles) of the amount of Cs^+ present.

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Stereocontrolled and Regiocontrolled Addition of Two or Three Carbon Substituents across an Arene Double Bond of Phenyloxazolines and Phenylmethanimines Coordinated to the Tricarbonylchromium Group

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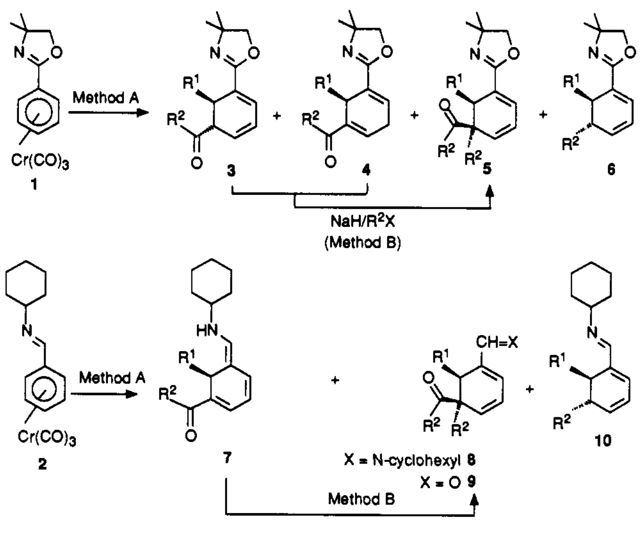
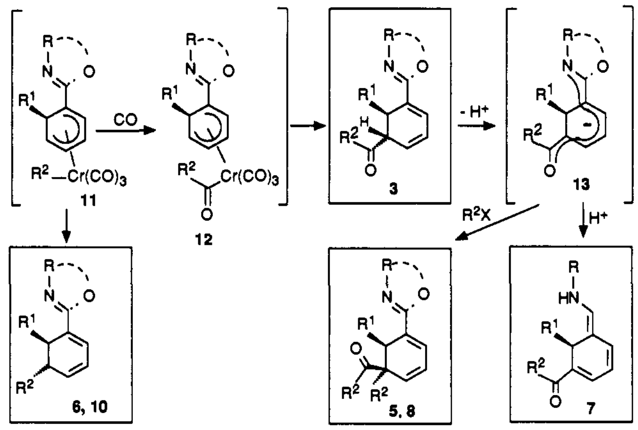
The regio- and stereocontrolled addition of substituents across an arene double bond is an attractive route to substituted alicyclic rings. Available methods are based on the activation of the arene to the first, nucleophilic, addition. Reaction of the intermediate with a carbon electrophile then introduces the second substituent.[1] Both σ-bound groups, such as oxazolines[2] and imines,[3] and the π-bound group $Cr(CO)_3$[4] activate naphthalenes[2a-e,3,4a-c] and pyridines[2f,g,4d-f,5] to the sequential nucleophile/electrophile addition, but only the $Cr(CO)_3$ group appears to be able to also activate benzene and its derivatives to the double addition. The reaction proceeds via nucleophilic addition to the exo face of the complexed arene,[6] followed by alkylation of the anionic cyclohexadienyl complex intermediate at the metal center, CO insertion, and acyl migration to the endo face of the cyclohexadienyl ligand (reductive elimination) to give, after facile metal removal, the product of a 1,2-trans alkyl/acyl addition.[7] We found that the tricarbonylchromium phenyloxazoline and phenylmethanimine complexes **1** and **2** undergo highly regioselective ortho addition of carbon nucleophiles.[8] In this paper we describe the unexpected

Scheme I



Scheme II



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(1) For examples of alternative organometallic methodologies involving a second nucleophilic addition either to a cyclohexadienyl ligand or to a carbonyl ligand, see: (a) Astruc, D. *Synlett* **1991**, *6*, 369. (b) Pike, R. D.; Sweigart, D. A. *Synlett* **1990**, *10*, 565. (c) Padda, R. S.; Sheridan, J. B.; Chaffee, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1226.

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(5) With pyridines, the second step is N-alkylation or -acylation.

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Table I

entry	complex	R^1Li	R^2X	method[a]	product distribution (% yield)[b]			
1	**1**	MeLi	MeI	A[c]		**4a** (10)[d]	**5a** (45)	**6a** (6)
2	**1**	MeLi	MeI	B[c]			**5a** (52)	**6a** (6)
3	**1**	MeLi	EtI	A	**3b** (22)	**4b** (10)[d]	**5b** (51)	
4	**1**	MeLi	EtI	B			**5b** (62)	
5	**1**	MeLi	$PhCH_2Br$	A		**4c** (15)		**6c** (54)
6	**1**	MeLi	AllylBr	A	**3d** (20)[d]			**6d** (65)
7	**1**	nBuLi	AllylBr	A[e]	**3e** (19)			**6e** (64)
8	**1**	PhLi	AllylBr	A[e]	**3f** (19)[d]			**6f** (67)
9	**2**	MeLi	MeI	A		**7a** (73)	**8a** (9)	**10a** (8)
10	**2**	MeLi	MeI	B			**9a** (74)	**10a** (10)
11	**2**	MeLi	EtI	A		**7b** (45)	**8b** (6) + **9b** (21)	**10b** (3)
12	2	MeLi	AllylBr	A				**10c** (57)

[a] Method A: (1) R^1Li (1.1 equiv)/THF/−78 to −40 °C (or to −20 °C), 3 h. (2) HMPA (10 equiv)/R^2X (10 equiv)/CO (4 bar)/−78 to 20 °C overnight. Method B: same as A, then (3) NaH (3 equiv)/R^2X (10 equiv)/−78 to 20 °C, 4 h. [b] Yields refer to isolated material after flash chromatography. [c] HMPA was replaced by MeCN. [d] Estimated by ^1H NMR. [e] Reaction run under N_2 atmosphere.

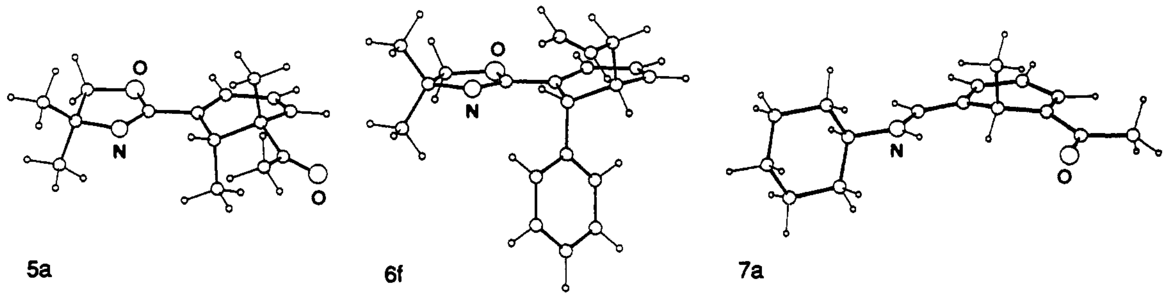

Figure 1. ORTEP structures of **5a**, **6f**, and **7a**.

results of tandem nucleophile/electrophile addition reactions to complexes **1** and **2**.

The sequential addition of an alkyl- or aryllithium reagent and a primary alkyl, allyl, or benzyl halide to complexes **1** and **2** led to cyclohexadienes **3–6** and **7–10** (Scheme I and Table I). A common feature of the products is the 1,5,6-substitution pattern, which indicates that C–C bond formation was highly regioselective.[9] With complex **1**, the alkyllithium/alkyl halide additions gave predominantly **5** with some of the initially expected product **3**, partially or completely isomerized to **4** (method A, entries 1 and 3). Treatment of the reaction mixture with an excess of NaH and electrophile (method B, entries 2 and 4) gave **5** exclusively. The one-pot reaction sequence introduces regio- and stereoselectively three C substituents across an arene double bond.[10] The cis arrangement between R^1 and the acyl group was established by an X-ray analysis of **5a** (Figure 1). Parallel results were obtained with the imine complex **2**, but in the absence of added base and alkylating agent, the unusual deep red enamine **7** (X-ray, Figure 1) was isolated as major product (entries 9 and 11). Treatment of **7a** with NaH and MeI gave, after hydrolysis, **9a** (entry 10).

Products **6a** and **10a,b** were very minor products in reactions with alkyl halides (3–10%). This changed entirely with allyl and benzyl halides. The resulting intermediates **11** (Scheme II) undergo reductive elimination without prior insertion of CO. Compounds **6c–f** (X-ray of **6f**, Figure 1) and **10c** were the major and sometimes exclusive products (entries 5–8, 12).[11] As analogous reactions with $(C_6H_6)Cr(CO)_3$ (with methyldithiane as nucleophile, allyl or benzyl bromide as electrophile) always give acyl products only, the unprecedented formation of products without CO insertion must be attributed to the electron-withdrawing effect of the oxazoline and imine substituents, which, via conjugation, increase the reactivity of the cyclohexadienyl metal carbon bond in **11** toward reductive elimination.[12] The same effect is responsible for the easy deprotonation of **3**. Regio- and diastereoselective C-alkylation from the less hindered face of the resulting delocalized enolate **13** takes place with soft electrophiles, affording **5** or **8**, whereas in reactions of the imine intermediate and the hard electrophile H^+, N-protonation gives **7**.[13]

In conclusion, the imine or oxazoline substituent directs nucleophilic addition to C(2) and the C-electrophile to C(3). In accord with the migratory aptitudes of the R^2 groups to carbonyl insertion (alkyl > methyl > benzyl, allyl),[14] either the acylcyclohexadienes **5** and **9** or the allylcyclohexadienes (benzylcyclohexadienes) **6** and **10** are formed in a one-pot reaction sequence with good selectivity.

Further studies including an asymmetric variant of this methodology are in progress.

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Supplementary Material Available: Spectroscopic (IR, ^1H NMR, MS) and analytical data for 21 isolated compounds (**3–10**) and results of X-ray studies of **5a**, **6f**, and **7a** including structures with atom numbering and tables of crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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(9) The 1,2-tandem nucleophile/electrophile addition to 1-naphthyloxazoline or 1-naphthylmethanimines and to 2-naphthyloxazoline gives 1,2-dihydronaphthalenes with a 1,1,2- and 1,2,2-substitution pattern.[2a-f,3a,b]

(10) Traces of a side product, which was tentatively identified as the epimer of **5a,b**, was detected in a few reactions (^1H NMR spectrum of the crude mixture). The diastereomeric ratios were always higher than 95:5.

(11) Yields of ketones **3d** and **3f** were determined by ^1H NMR analysis of the crude mixtures before flash chromatographic isolation of **6d** and **6f**. Attempts to direct the reaction of **1** exclusively to **6** by carrying out the reaction under N_2 rather than CO were not successful, and neither yields nor product distribution was affected.

(12) It is well established that reductive elimination of ketones from acyl–alkyl transition-metal complexes is a faster reaction than the reductive coupling of two alkyl ligands to form alkanes. See: (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613. (b) Saunders, D. R.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2132. (c) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003.

(13) The acidity of the N–H bond in **7** was evidenced by a fast proton–deuterium exchange in D_2O observed by ^1H NMR.

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