lengths (Table SIII), bond angles (Table SIV), anisotropic thermal parameters (Table SV), and H atom coordinates and isotropic thermal parameters (Table SVI) (10 pages); observed and calculated structure factors (Table SVII) (38 pages). Ordering information is given on any current masthead page.

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Extended Hückel Calculations and the Role of d Orbitals in Transition-Metal-Cluster Bonding

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Received February 12, 1986

In two recent articles in this journal, Woolley[1,2] has suggested that the metal d electrons play a crucial role in the bonding between transition-metal atoms in clusters and furthermore[2] that the extended Hückel (EH) model offers no explanation for the metal–metal bonding in such clusters. While the first statement would receive general support from chemists, the second is clearly more contentious. In the light of the important advances in our understanding of cluster chemistry furnished by Hoffmann,[3] Mingos,[4] and others[5] that have been supported by calculations of this type, it is desirable to examine the validity of Woolley's argument[2] in some detail. Some early EH calculations[5,6] suggested that the d bands in clusters were rather narrow, and this was interpreted in terms of the d electrons making a very minor contribution to the metal–metal bonding. It is the purpose of this note to demonstrate that a detailed examination of the results from a number of EH calculations can satisfactorily account for the bonding in such clusters and *indeed* does highlight the important contribution made by the metal d electrons. The relationship between the conclusions derived here and the qualitative predictions of Woolley[1,2] based on the methodology of metal physics will also be discussed. Finally it will be clearly demonstrated within the framework of perturbation theory how the symmetry of the ligand field induces an interplay between the metal s, p, and d electrons that is not present in the bare metal cluster. This enables an ambiguity, left unresolved in the metal physics predictions,[1,2] to be understood.

EH calculations[7] on the neutral bare metal clusters Fe_5 and Ru_5 (both trigonal bipyramidal)[8] and octahedral[8] Co_6 have been performed with the usual metal parameters[3,9] and Wolfsberg–Helmholtz constant ($K = 1.75$).[7] It must be emphasised that contrary to the claims of Woolley,[1,2] the parameters have not been deliberately "chosen" to give artificially high metal d–d overlap integrals. Thus for example in the case of Fe_5 all such values are 0.051 or less, consistent with the ideas of metal physics. The calculations show that the atomic d orbitals overlap to give a band of $5n$ levels (for an M_n cluster) of width 1.7–3.0 eV. These are also of the order considered reasonable by Woolley (at least 2.2 eV)[1] for metal d bands in bare metal clusters. (The introduction of a ligand shell leads to an increase in d-band width as discussed below.) In each case the overlap of the valence s and p orbitals is larger as a consequence of their greater spatial extension giving a much wider spread of levels. One of these, derived from metal s orbitals (which we shall call S_8^σ in the notation of tensor surface harmonic theory,[10] TSH), lies embedded in the d band, and the other $4n - 1$ levels lie well above the d band. Clearly the exact nature of the metal–metal bonding will depend on whether S_s^σ lies above or below the Fermi level of the cluster. With any reasonable EH parameterization, S_8^σ and the Fermi level are very close in energy, and in Table I we summarize the percentage contribution of each type of orbital overlap to the computed Mulliken overlap population for the three clusters, assuming first that S_s^σ lies above and second that it lies below the Fermi level. In each case the s–s, s–p and p–p orbital overlaps make a relatively minor (0–36%) contribution to the metal–metal bonding (in Woolley's view[1,2] the valence s and p orbitals actually give rise to a small antibonding contribution), and the major component of the metal–metal bonding arises from interactions involving the metal d orbitals. This is contrary to the impression given elsewhere[5,6] that EH calculations ascribe the metal–metal bonding to overlap between s and p orbitals. Further indication of the minor role ascribed to the s and p orbitals by the EH method comes from the calculated atomic orbital populations. If the S_s^σ level is assumed to be unoccupied, these are, for example

$$Fe_5 \quad s^{0.29}\, d^{7.63}\, p^{0.09}$$

$$Ru_5 \quad s^{0.12}\, d^{7.82}\, p^{0.06}$$

and even if the S_8^σ level is assumed to be occupied there is relatively little change. For example, the calculations give

$$Fe_5 \quad s^{0.52}\, d^{7.39}\, p^{0.09}$$

Table I. Percentage of Total Overlap Population Arising from Overlap between Individual Sets of Metal Atomic Orbitals for a Series of Pentanuclear Clusters[a]

	percentage of total overlap population arising from each type of orbital overlap					
cluster	s–s	s–p	p–p	s–d	p–d	d–d
Fe_5 (S^σ vacant)	11	2	0	30	22	35
Fe_5 (S^σ occupied)	29	2	0	21	19	29
Ru_5 (S^σ vacant)	−1	−2	−1	34	24	45
Ru_5 (S^σ occupied)	30	0	0	19	13	39
Co_6 (S^σ vacant)	0	1	−1	40	42	19
Co_6 (S^σ occupied)	36	3	0	21	22	18
Fe_5^{32-}	1	30	73	5	0	−9
$Fe_5X_5^{22-}$	11	37	54	5	3	−9
$Fe_5X_{15}^{2-}$	10	22	21	10	29	9
$Fe_5(CO)_{15}^{2-}$	3	11	18	13	40	16

[a] A negative value indicates an antibonding contribution to the metal–metal-overlap population.

Consider now the introduction of a set of ligands to such a cluster. The electron count of the resulting species may be predicted by using the criterion of Lauher;[5] viz., there will be a large energy gap between the cluster HOMO and LUMO in the region close to the p orbital energy in an isolated atom. This gives total electron counts of 72 and 86, respectively, for the trigonal bipyramid and the octahedron as is well-known.[4] In a 72-electron cluster such as $Fe_5X_5^{22-}$, (where X represents a two-electron ligand with the orbital exponent and H_{ii} of hydrogen),[9] the cluster d band orbitals do not interact significantly with the ligands, and complete occupation of the d band gives a net antibonding contribution to the metal–metal interaction. In this case, and in this highly

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(1) Woolley, R. G. *Inorg. Chem.* **1985**, *24*, 3519.
(2) Woolley, R. G. *Inorg. Chem.* **1985**, *24*, 3525.
(3) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711 and references therein.
(4) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
(5) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.
(6) Mingos, D. M. P. *J. Chem. Soc. A* **1974**, 133.
(7) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
(8) Bond lengths (Å) used in the calculations: Fe–Fe = 2.53; Ru–Ru = 2.854; Co–Co = 2.50; Fe–X = 1.60.
(9) EH parameters: Fe 4s $\zeta = 1.90$, $H_{ii} = -9.17$ eV; 4p $\zeta = 1.90$, $H_{ii} = -5.37$ eV; 3d $\zeta_1 = 5.35$ ($c_1 = 0.5366$), $\zeta_2 = 1.80$ ($c_2 = 0.6678$), $H_{ii} = -12.70$ eV; Ru 5s $\zeta = 2.078$, $H_{ii} = -8.00$ eV; 5p $\zeta = 2.043$, $H_{ii} = -4.3$ eV; 4d $\zeta_1 = 4.21$ ($c_1 = 0.5772$), $\zeta_2 = 1.95$ ($c_2 = 0.5692$), $H_{ii} = -12.20$ eV; Co 4s $\zeta = 2.00$, $H_{ii} = -9.21$ eV; 4p $\zeta = 2.00$ $H_{ii} = -5.29$ eV; 3d $\zeta_1 = 5.55$ ($c_1 = 0.5679$), $\zeta_2 = 2.10$ ($c_2 = 0.6059$), $H_{ii} = -13.18$ eV; X 1s $\zeta = 1.30$, $H_{ii} = -13.60$ eV.
(10) Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563.

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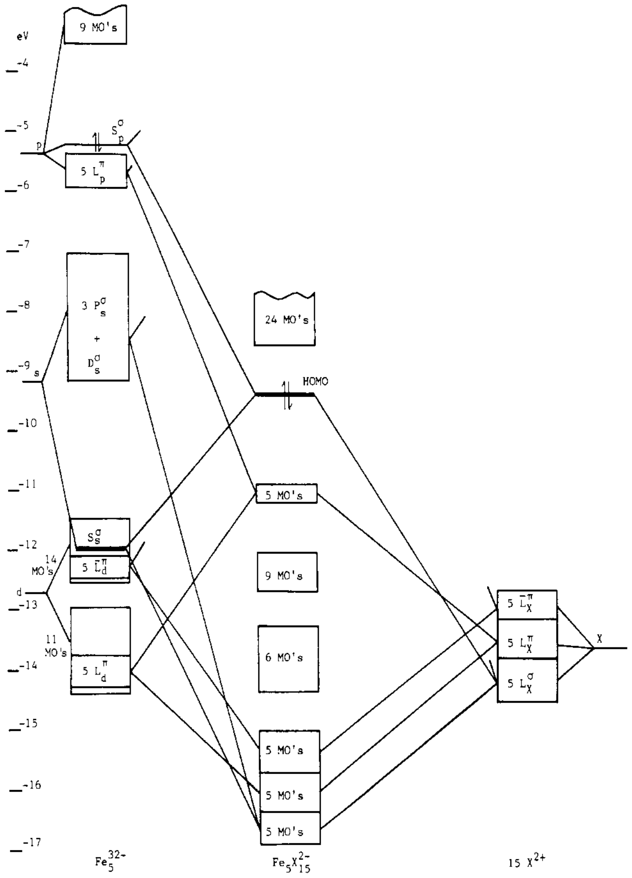

Figure 1. Schematic MO diagram for the formation of $Fe_5X_{15}^{2-}$ from a bare metal Fe_5 cluster. The lowest 15 MO's of the cluster are Fe–X bonding. Six of the corresponding Fe–X antibonding MO's are stabilized for occupation by second-order mixing with the Fe_5 S_p^σ and L_p^π MO's, becoming strongly metal–metal bonding and metal–ligand nonbonding in the process, while the remaining nine Fe–X antibonding MO's are also metal–metal antibonding and remain unoccupied. Thus the cluster contains 72 valence electrons.

artificial case alone, is it true to say that EH calculations predict that the metal–metal bonding arises totally from overlap between metal s and p orbitals (see Table I).

If however we consider the introduction of a realistic number of ligands around a cluster so that the idealized local symmetry about the metal atoms is reduced from $C_{\infty v}$, then the situation is very different. Consider the case of $Fe_5X_{15}^{2-}$, with three terminal ligands on each atom. As shown schematically in Figure 1 the metal orbitals in a bare Fe_5 cluster give rise to the following combinations in the notation of TSH:

	metal–metal bonding	metal–metal antibonding
s	S_s^σ	$3P_s^\sigma + D_s^\sigma$
p	$S_p^\sigma + 3P_p^\pi + 2D_p^\pi$	$3P_p^\sigma + D_p^\sigma + 2\bar{D}_p^\pi + 3\bar{P}_p^\pi$
d	$S_d^\sigma + 3P_d^\pi + 2D_d^\pi + 5D_d^\delta$	$3P_d^\sigma + D_d^\sigma + 2\bar{D}_d^\pi + 3\bar{P}_d^\pi + 5\bar{D}_d^\delta$

The ligand σ-donor orbitals give rise to the following combinations:

$$S_X^\sigma + 3P_X^\sigma + D_X^\sigma + 3P_X^\pi + 2D_X^\pi + 2\bar{D}_X^\pi + 3\bar{P}_X^\pi$$

The five L_X^σ (L = S, P, etc.) orbitals interact predominantly with the five L_s^σ orbitals, giving rise to five Fe–X bonding MO's. One of the five antibonding components of this first-order interaction (derived from the metal–metal bonding S_s^σ combination) is strongly stabilized by second-order mixing with the higher lying S_p^σ level, becoming more strongly metal–metal bonding and approximately metal–ligand nonbonding. This is the HOMO of the resulting cluster. The other four components of the first-order interaction do not enter into analogous three-orbital–four-electron interactions with the L_p^σ (L = P, D) orbitals since the latter are strongly metal–metal antibonding and therefore lie too high in energy.

The five L_X^σ orbitals interact predominantly with the five metal–metal-bonding L_d^π orbitals from the d band giving five Fe–X bonding MO's. The five Fe–X antibonding components of this first-order interaction are stabilized by mixing with the five metal–metal-bonding L_p^π orbitals, again becoming strongly metal–metal bonding and approximately metal–ligand nonbonding. The five $\bar{L}_X^\pi$ orbitals interact with the five metal–metal antibonding $\bar{L}_d^\pi$ orbitals from the d band giving five further Fe–X bonding MO's. In this case the Fe–X antibonding combinations that are also Fe–Fe antibonding are not sufficiently stabilized by second-order mixing with the five Fe–Fe antibonding $\bar{L}_p^\pi$ orbitals, which lie too far apart in energy and remain unavailable for occupation. The remaining 15 d-band orbitals ($S_d^\sigma + 3P_d^\sigma + D_d^\sigma + 5D_d^\delta + 5\bar{D}_d^\delta$) remain almost unaffected by interaction with the σ-donor ligands.

In this way the metal–metal antibonding contribution of the $3P_d^\sigma + D_d^\sigma + 3\bar{P}_d^\pi + 2\bar{D}_d^\pi$ orbitals of the d band is reduced since their occupied combinations with the ligand orbitals lie predominantly on the latter and are strongly metal–ligand bonding. The metal–metal-bonding contribution of the $S_d^\sigma + 3P_d^\pi + 2D_d^\pi$ orbitals is however retained since both Fe–X bonding and antibonding combinations are occupied. Indeed the mixing of the latter with $S_p^\sigma + 3P_p^\pi + 2D_p^\pi$ orbitals enhances the metal–metal overlap.

In conclusion therefore the effect of the ligands is 2-fold: first, to mitigate some of the antibonding contribution from the d band in Fe_5^{32-} or $Fe_5X_5^{22-}$; second, to induce a hybridization of metal d and p orbitals to maximize both metal–metal and metal–ligand bonding.

It is clear therefore that one would not expect the bonding in a cluster such as $Fe_5X_{15}^{2-}$ to exactly parallel that in a bare metal Fe_5 cluster and that the effect of the ligands is to cause a greater bonding role for the metal p orbitals in the $Fe_5X_{15}^{2-}$ cluster. As shown in Table I, however, it is clear that the EH method does not ascribe the metal–metal bonding in such a cluster to s–s and s–p overlap alone. The d orbitals are calculated to play a significant role in $Fe_5X_{15}^{2-}$ and even more in $Fe_5(CO)_{15}^{2-}$, where the carbonyl π^* orbitals stabilize additional metal-based orbitals.

The predictions of Woolley[1,2] are consistent with the above analysis with but one exception. Thus Woolley's analysis would suggest that the five L_d^π orbitals do not interact with the ligand orbitals and remain purely metal–metal bonding and that the five L_X^π orbitals instead interact directly with the five L_p^π orbitals in two-orbital–two-electron interactions as opposed to the $L_d^\pi/L_X^\pi/L_p^\pi$ three-orbital–four-electron interactions proposed here. Within the framework of perturbation theory, the former situation can only pertain if the L_d^π/L_X^π interaction is not feasible on the grounds of orbital energy match or overlap criteria. Clearly the L_d^π/L_X^π energy match is far more favorable than that for the L_p^π and L_X^π orbitals, and Woolley himself has stated[1] that the metal d and ligand orbitals hybridize strongly in his discussion of why the metal d-ligand antibonding orbital $A_{2u}(1)$ in the octahedral $M_6(\mu_3\text{-}X)_8$ cluster is so highly destabilized. Clearly the exact quantitative contribution of the L_p^π orbitals to the metal–metal bonding will vary from cluster to cluster, but it is difficult, in terms of perturbation theory, to envisage a situation where this contribution would be negligible. It therefore seems reasonable that there will indeed be a considerable d–p hybridization in ligated metal clusters and that the introduction of the ligand shell around a bare metal cluster leads to a considerable modification of the metal–metal bonding.

One further point concerns Woolley's criticism of the inability of the EH method to give d-band widths in accord with experiment. In the case of $Fe_5X_{15}^{2-}$, if the d band is assumed to comprise only the 15 metal–ligand nonbonding d MO's its width is 2.3 eV, while if the five $L_d^\pi/L_X^\pi/L_p^\pi$ skeletal bonding MO's [which have considerable (51–58%) d character] are included in the d band (as they are, albeit in a different context, in the Woolley view), the d-band width is 3.5 eV. Such values are of the order considered reasonable by Woolley in the light of experimental measurements.

In his discussion Woolley poses, but leaves unresolved, the question of how the orbitals of the constituent fragments [5 ×

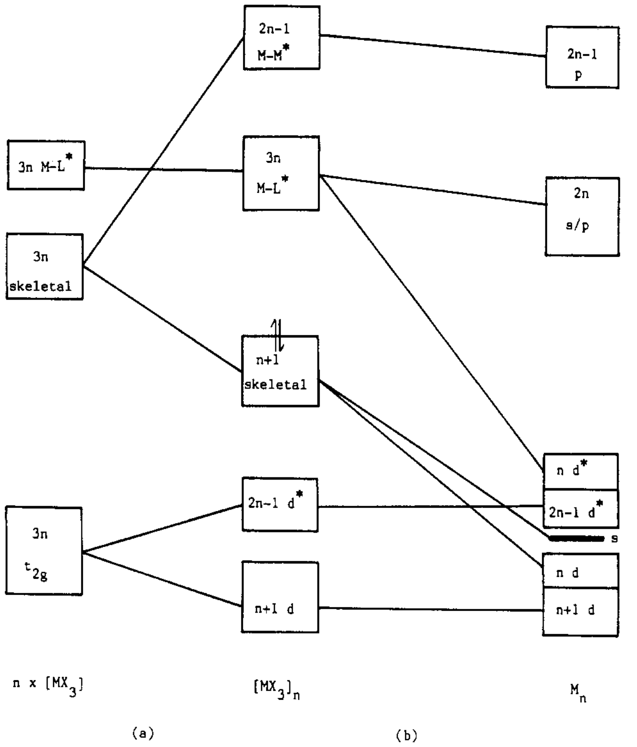

Figure 2. Schematic illustration of the correlation of the metal-based orbitals of an $[MX_3]_n$ cluster with (a) $n[MX_3]$ fragments and (b) a bare metal M_n cluster. The $(n + 1)$ skeletal electron pairs expected from the polyhedral skeletal electron pair theory are derived predominantly from the metal–metal-bonding orbitals in the s and d bands. The skeletal MO's are stabilized in the actual cluster by mixing in $(n + 1)$ of the $2n$ s/p MO's of M_n (not shown in the figure).

FeX_3 in this case] correlate with those of the final cluster, in the context of the isolobal analogy. In particular, Woolley states that the metal physics view would predict two metal–ligand antibonding orbitals with the totally symmetric representation. Woolley suggests that one of these will be derived from the in phase combination of the radial skeletal bonding hybrids of the FeX_3 fragments and therefore from the borane analogy would be expected to be strongly metal–metal bonding, but in the metal physics view this orbital may be expected to lie above E_{HOMO}. Such an orbital must clearly be occupied to give a closed-shell configuration for an 86-electron octahedron or a 72-electron trigonal bipyramid. Figure 1 clearly shows however that the "mystery" orbital is simply the central component of the S_s^σ/S_x^σ/S_p^σ three-orbital interaction and is therefore metal–ligand nonbonding but metal–metal bonding, in accord with the isolobal analogy. Woolley is incorrect to imply however that the borane analogy requires that this orbital should be the most strongly bonding of the skeletal electron pairs. Since the energy level ordering of the frontier orbitals of BH (radial below tangential) and $M(CO)_3$ is reversed, it is entirely to be expected that the S^σ skeletal orbital should be the most strongly bonding for B_nH_n and yet the HOMO for $[M(CO)_3]_n$. Thus the confusion arising out of the qualitative metal physics predictions is clearly resolved in the light of EH calculations.

Although the specific EH calculations reported here in detail have been for Fe_5 clusters, further calculations on other systems have shown the bonding description given here to be general. Thus for any M_n cluster there will be $(n + 1)$ metal–metal-bonding MO's derived from the p orbitals (one S_p^σ and n L_p^π). Thus there will be $(n + 1)$ three-orbital–four-electron interactions, the central component of each corresponding to the (n + 1) skeletal electron pairs expected from the polyhedral skeletal electron pair theory. It is important to recognize that it is the ligand-induced participation of the $(n + 1)$ *bonding* levels of the p band in such three orbital interactions which dictates the observed number of skeletal electron pairs. For an M_nX_x cluster there will be x M–X bonding MO's [formed from n L_s^σ and $(x - n)$ L_d^π and $\bar{L}_d^\pi$ orbitals], $(6n - x)$ d band MO's and $(n + 1)$ skeletal bonding MO's. For the case of an $[MX_3]_n$ cluster, derived from n conical MX_3 fragments, the way in which the orbitals of the cluster correlate with those of (a) n MX_3 fragments and (b) M_n and X_{3n} fragments is illustrated in Figure 2. There are a total of $(7n + 1)$ occupied MO's. It is the contention of this paper that the arrangement of these levels can be most effectively rationalized in the context of the EH method rather than *qualitative* predictions based on the methodology of metal physics.

Acknowledgment. I am grateful to Dr. P. W. Fowler and a reviewer for useful comments.

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Catalytic H-D Exchange in Deuteriated Alcohols Promoted by Early-Transition-Metal Alkoxides. Insight into a Mechanistic Puzzle[1]

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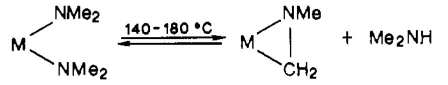
Received March 25, 1986

Several years ago[2] we reported that early-transition-metal dialkylamides catalyze exchange between the N–H and C–H hydrogens of dimethylamine-*N*-*d*. The reaction was demonstrated to involve the reversible metalation of the dimethylamide ligand (eq 1). Since this observation led to the development of an unprecedented type of catalytic C–C bond-forming process,[2] we wished to explore the generality of such H–D exchange reactions and in particular whether alcohols might be similarly activated.



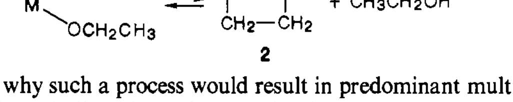
(1)

Catalytic H–D exchange in alcohols required elevated temperatures (180–220 °C). Nevertheless, heating ethanol-*d* in the presence of 1 mol % of the ethoxides of Nb, Ta, or Zr did result in exchange as indicated by the appearance of the OH resonance in the ^1H NMR spectrum. To our surprise, the deuterium was not scrambled into the α-position of the ethanol by analogy to eq 1. Instead, ^2H NMR showed exclusive incorporation of deuterium into the methyl group[3] (eq 2). By taking advantage of

$$\mathrm{CH_3CH_2OD} \xrightarrow[\mathrm{M\,=\,Zr,\,Nb,\,Ta}]{\mathrm{M(OEt)}_m} \underset{\mathbf{1}}{\mathrm{CD}_n\mathrm{H}_{3-n}\mathrm{CH_2OH(D)}} \qquad (2)$$

the isotopic shift effect in the ^2H NMR, it was possible to distinguish between deuterated products containing one, two, or three ^2H atoms in the methyl group. As summarized in Table I, even at low conversions, much of the product consisted of di- and trideuteriated ethanols (**1**; $n = 2$ or 3).

This observation complicates the mechanistic interpretation of eq 2. Although reversible cyclometallation according to eq 3 would explain the exclusive activation of the methyl hydrogen, it is not apparent why such a process would result in predominant multiple deuteration. (Alkoxide exchange with free alcohol is known to be rapid.[2]) Moreover, oxametalacycle **2** is expected to decompose



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[1] Contribution No. 4012.

[2] Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161-162.

[3] This situation represents a striking contrast with the scrambling of deuterium of CH_3CH_2OD exclusively onto the methylene carbon, which is promoted by low-valent group 8 catalysts: Regan, S. L. *J. Org. Chem.* **1974**, *39*, 260-261. Sasson, Y.; Blum, J. *J. Chem. Soc.*, , *Chem. Commun.* **1974**, 309-310.

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