Thus there are only two sets of M–C distances in the molecular anion; the shorter averages to 1.95 (2) Å and the longer [the Mo–C distance to equatorial carbonyls trans to each other] averages to 2.05 (2) Å. It should be stated that there are no significant intermolecular or interionic interactions which might influence molecular geometry.

Appropriate and interesting comparisons may be made between disubstituted, dinuclear species containing full metal–metal bonds and the title compound. Phosphine ligands are attached *diaxially* in the staggered dimers $[Mn(CO)_4L]_2$ ($L = PMePh_2$,[13] PPh_3,[14] $AsPh_3$,[14] and PEt_3[15]). Although the less bulky (aided by a longer M–L bond) $AsMe_2Ph$ ligands are attached *diequatorially* in eclipsed $[Mn(CO)_4(AsMe_2Ph)]_2$,[13] the As(1)–Mn(1)–Mn(2)–As(2) torsion angle is around 180°; i.e., the ligands are on opposite sides of the molecule. Earlier solid-state structural studies of VIB bridging hydride complexes have shown an impressive ease of interconversion between bent and linear forms of μ-$H[W(CO)_5]_2^-$.[16,17] For that anion a simple change in counterion from Et_4N^+ to PPN^+ or PPh_4^+ effects a change in molecular anion structure from (linear, eclipsed) to (bent, staggered), respectively. (Notably the bending leads to a decrease in W–W distance of ~0.15 Å.) If steric factors only dictated the structure of μ-$H[Mo_2(CO)_9PPh_3]^-$ or μ-$H[Mo(CO)_4(PMePh_2)]_2^-$, then we would expect a linear geometry with substituents positioned to minimize interactions, analogous to the manganese dimers. The observed geometry defined above for μ-$H[Mo(CO)_4(PMePh_2)]_2^-$ strongly suggests that this anion actually profits from steric interactions. Not only does the greater electron-donating ability of the two substituents provide for greater Mo–Mo overlap in the three-center, two-electron bridged hydride bond,[18] as compared to the μ-$H[Mo_2(CO)_9PPh_3]^-$ case, but the positioning of both substituents on the same side of the molecular anion allows for steric strain to be applied to greatest advantage with regards to the Mo···Mo interaction.

Finally, the orientation of the phosphine methyl groups towards the X grouping suggested the possibility of linking the phosphorus donor sites. Reactions of Et_4N^+ μ-$H[Mo(CO)_5]_2^-$ with $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2, 3$) have yielded nicely crystalline, yellow, carbonyl-containing salts. Elemental analyses as well as infrared and NMR data suggested these salts to contain phosphine substituted, bridging hydride, dinuclear anions, analogous to the title anion, i.e.,

$$\mu\text{-}H[(OC)_4Mo \leftarrow PPh_2(CH_2)_nPh_2P \rightarrow Mo(CO)_4]^-$$

The bridging diphos ligands are apparently much less labile than the monodentate ligands. For example, Et_4N^+ μ-$H[Mo(CO)_4)PMePh_2]_2^-$ in refluxing THF solution reacted with CO in a matter of minutes to produce μ-$H[Mo_2(CO)_9PMePh_2]^-$ and, over the course of a day, to produce μ-$H[Mo(CO)_5]_2^-$. The propylenediphos linked dinuclear anion however under similar reaction conditions showed no production, of μ-$H[Mo_2(CO)_9PPh_2(CH_2)_3PPh_2]^-$, but rather a slow production (slower by a factor of 2 than the analogous reaction described above) of μ-$H[Mo(CO)_5]_2^-$ was obtained.

Currently, chemical studies of these systems are being extended to include protonation and other reactions which would probe the hydride functionality.

Acknowledgment. The authors appreciate the receipt of data from Professor J. L. Petersen prior to publication as well as helpful discussion with Professor D. J. Darensbourg. The financial support of Tulane University (M.Y.D.) and the National Science Foundation (J.L.A.) is acknowledged.

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Intermolecular Reduction of Coordinated Ligands by Transition Organometallic Hydride Reagents

Sir:

Transition organometallic hydride complexes[1] are of immense importance to the development of organometallic chemistry. Their most prevalent reactivity mode, alkene insertion,[2] corresponds to a concerted addition of a metal hydride across a substrate multiple bond within the same coordination sphere. Intermolecular modes of reactivity are also available and entail either proton transfer,[3] hydrogen atom donation,[4] or nucleophilic attack by the metal–H bond.[5] Relatively little, however, is known of the formal transfer of hydride from a transition organometallic hydride complex to an electrophile, irrespective of their hydridic nomenclature and the localization of negative charge on the hydrogen end of neutral metal carbonyl hydrides.[6] Both trityl carbocation[7a,b] and the proton[7b,c] abstract hydride from the limited number of transition metal hydrides examined. Several early transition metal hydride complexes $Cp_2Zr(H)X$ ($X = Cl, R$;[8a] $Cp = \eta^5$-C_5H_5), $(\eta^5$-$C_5Me_5)_2ZrH_2$,[8b] and Cp_2NbH_3[8c] additionally transfer hydride to water, organic ketones, and even coordinated CO.

We now report that first row, group 8 transition organometallic hydride reagents effect intermolecular hydride addition to coordinated alkene and carbene ligands. The readily available $CpFe(CO)Ph_3P(H)$[9] quantitatively reduces, as evidenced by IR monitoring, several $CpFe(CO)_2$-η^2-alkene salts

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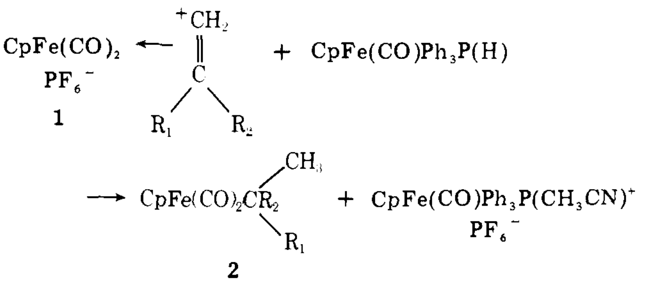


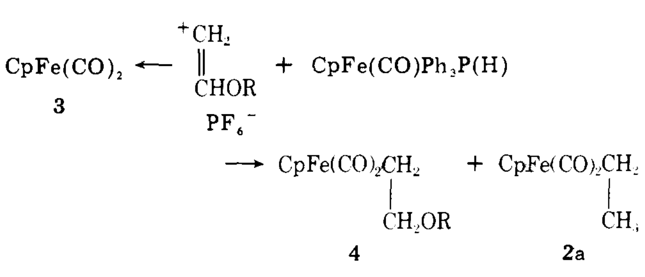
a, R_1, R_2 = H; b, R_1 = H, R_2 = CH_3; c, R_1, R_2 = CH_3

(**1**)[10] to their η^1-alkyl counterparts (**2**) at room temperature.[11] Treatment of the ethylene (**1a**), propylene (**1b**), and isobutylene (**1c**) η^2-alkene salts in CH_3CN with 1 equiv of $CpFe(CO)Ph_3P(H)$ affords, after a 0.5-h reaction time followed by petrol extraction and column chromatography, the ethyl (**2a**), isopropyl (**2b**), and *tert*-butyl (**2c**) η^1-alkyl complexes, respectively, in 90% yields. Further workup of the reaction mixture also produces the $CpFe(CO)Ph_3P(CH_3CN)^+$ solvate[13] in 70% yield.

These reactions are noteworthy for (1) a high regiospecificity corresponding to exclusive (within NMR detection limits) hydride addition at the less substituted vinyl carbon and (2) an absence of the dimeric byproduct $[CpFe(CO)_2]_2$. Borohydride reagents, in contrast, generally reduce the η^2-alkene salts **1b** and **1c** to different regioisomeric mixtures of isopropyl/*n*-propyl ($NaBH_4$, 1:3;[14a,c] $NaBH_3CN$, isopropyl only[14d]) and of isobutyl/*tert*-butyl ($NaBH_4$, 1:3;[14b] $NaBH_3CN$, isobutyl only[14d]) η^1-alkyl complexes. Borohydride reactions also frequently engender reduction at the iron site and generation of $[CpFe(CO)_2]_2$.[15a]

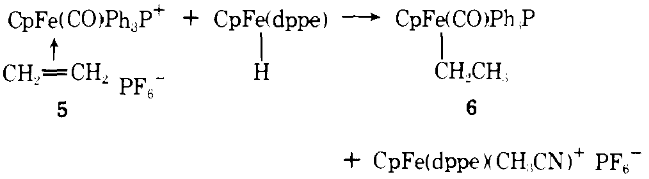
Since $CpFe(CO)Ph_3P(H)$ does not react with free ethylene under the above conditions,[9b] its reduction of the η^2-alkene compounds (**1**) necessarily entails activation of the alkene. A mechanism with the Fe–H bond undergoing nucleophilic attack[16] on the coordinated alkene of **1**, followed by elimination of the coordinatively unsaturated $CpFe(CO)Ph_3P^+$, is consonant with the substituent effects presented and with the established facility of nucleophilic addition to **1**.[15b]

The direction of hydride addition to unsymmetrically substituted $CpFe(CO)_2$-η^2-alkene cations need not occur only at the unsubstituted vinyl carbon. Thus, the η^2-vinyl ether salts **3**[17a] consume 1 equiv of $CpFe(CO)Ph_3P(H)$ and produce 1:1 mixtures of the η^1-2-alkoxyethyl (**4**) and η^1-ethyl (**2**a) complexes. Both products derive from hydride addition at the substituted vinyl carbon, in concordance with its partially localized positive charge.[17b] Hydride addition to the unsubstituted vinyl carbon would generate a η^1-α-alkoxyethyl complex, $CpFe(CO)_2$–$CH(OR)CH_3$, that would have been detected; see below. Treatment of **3b** with 1 equiv of $Ph_3PMe^+BH_4^-$ gives 50% conversion into the ethyl complex **2a**, while $LiB(Et)_3H$ in tetrahydrofuran affords a 90% yield of **4b**.

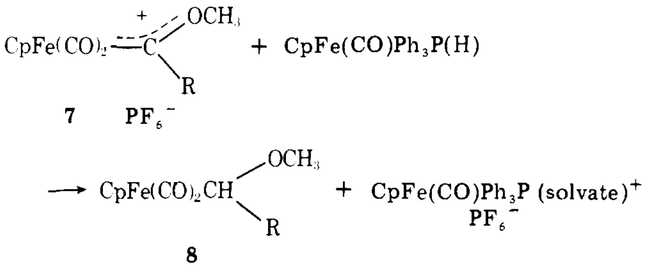


a, R = CH_3; b, R = CH_2CH_3

Transition metal hydride reduction of the η^2-ethylene compound $CpFe(CO)Ph_3P(CH_2{=}CH_2)^+$ (**5**) further demonstrates the importance of electronic control of these hydride transfer reactions. The η^2-ethylene compound **5** is less electrophilic than **1a** owing to Ph_3P replacement of a CO ligand.[18a] Accordingly **5** reduces to the corresponding η^1-ethyl complex **6**[20c] very slowly ($t_{1/2}$ = 6 h at room temperature, by IR) with $CpFe(CO)Ph_3P(H)$ as the hydride donor. Employment of the more electron-rich iron hydride $CpFe(dppe)H$[18] in 1:1 CH_2Cl_2-CH_3CN, however, leads to rapid (15 min) conversion of **5** into **6** and formation of the known solvate $CpFe(dppe)(CH_3CN)^+$.[18b]

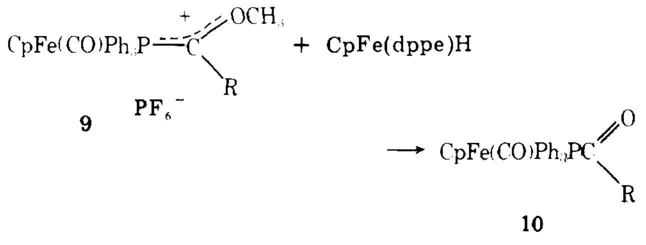


Transition organometallic hydride reagents also transfer hydride to the secondary[19a] and tertiary alkoxycarbene compounds **7**.[19] Alkoxycarbene compounds **7a–c** quantitatively consume (as judged by IR monitoring) 1 equiv of $CpFe(CO)Ph_3P(H)$ within 0.5 h in 1:1 CH_2Cl_2-CH_3NO_2. Workup of these reactions provides the η^1-α-alkoxyalkyl complexes **8** in high yield, with no evidence (via NMR) of further reduction to $CpFe(CO)_2R$ (R = CH_3, CH_2CH_3, CH_2Ph). Borohydride reduction of **7a**, in contrast, affords mixtures of the alkoxymethyl (**8**a) and methyl $CpFe(CO)_2CH_3$ complexes.[19a]



a, R = H; b, R = CH_3; c, R = Ph

Phosphine substituted secondary[19a] and tertiary[20] alkoxycarbene compounds **9** do not reduce to the η^1-α-alkoxyalkyl complexes with transition metal hydrides. Instead **9a,b** remain unaltered by $CpFe(CO)Ph_3P(H)$, while suffering dealkylation with $CpFe(dppe)H$. The secondary methoxycarbene compound **9**a and $CpFe(dppe)H$ thus produce an equimolar mixture of $CpFe(CO)_2Ph_3P^+$ and $CpFe(CO)Ph_3P$-CH_2OCH_3, that can be ascribed to intermediacy of the η^1-formyl complex **10**a. A stable acetyl complex **10b** results from the analogous dealkylation of **9b**. These results correspond to nucleophilic dealkylation of **9**,[19a,20] even though borohydride effects their reduction to η^1-alkyl and α-alkoxyalkyl complexes.



a, R = H; b, R = CH_3

Transition organometallic hydrides clearly enjoy the capability of effecting overall hydride transfer to coordinated ligands on another metal. Further studies will probe the influence of structure (mononuclear, binuclear, or cluster), charge, and stereoelectronic attributes of ancillary ligands on the hydride donating capacity of organometallic hydride complexes. Similar parameters also need to be investigated regarding the hydride-abstracting ligands, and suitably activated CO represents but one kind of ligand for which fixation by transition metal hydride reagents merits interest. Work is in progress along these lines.

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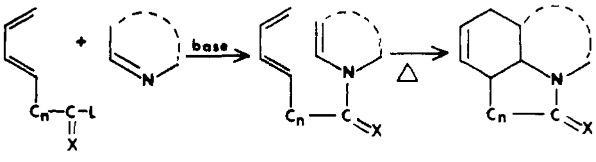
General Methods for Alkaloid Synthesis via Intramolecular [4 + 2] Cycloaddition Reactions of Enamides. A New Approach to the Synthesis of *Aspidosperma* Alkaloids

Sir:

Since substituted hydroindole and hydroquinoline rings are structural elements common to a diverse array of alkaloid natural products, a general synthetic strategy which could be employed for the facile assemblage of functionalized representatives of these important heterocyclic synthons would be highly useful. One entry to these ring systems which seems particularly attractive is depicted in eq 1 and features the intramolecular [4 + 2] cycloaddition reaction of an enamine or an enamide with a suitable diene partner. An important aspect of this novel approach to hydroindoles and hydroquinolines is the ease with which the requisite enamino dienes **3** (X = H_2) and enamido dienes **3** (X = O) may be constructed via a carbon–nitrogen bond forming process in which the imine **2** is coupled with a dienoic alkylating or acylating agent **1.** While there exist numerous examples of bimolecular[1] and intramolecular[2,3] Diels–Alder reactions of dienamides with various dienophiles as well as bimolecular [4 + 2] cycloadditions of enamines with electron-deficient dienes,[4] there appears to be only a single report of the [4 + 2] cycloaddition reactions of enamines or enamides with *unactivated* dienes.[5,6] We now report that endocyclic enamido dienes related to **3** (X = O; *n* = 1) and **3** (X = O; *n* = 2) undergo smooth, intramolecular [4 + 2] cycloadditions to give fused hydroindole and hydroquinoline derivatives, respectively.



(1)

1 2 3 4

X = H_2; O

n = 1;2

To evaluate the feasibility of utilizing intramolecular [4 + 2] cycloaddition reactions for the efficient construction of the hydrolulolidine ring system that is characteristic of the *Aspidosperma* alkaloids and also the hydrojulolidine skeleton which is representative of the *Lycopodium* alkaloids,[7] our attention was initially focused upon an investigation of the thermal chemistry of the enamido dienes **8**a–c and their homologues **11a,b.** Although the direct coupling of 3,4,5,6-tetrahydropyridine (**5a**)[8] with 3,5-hexadienoyl chloride gave only exiguous yields of the enamido diene **8a**, the formation of the requisite carbon–nitrogen bond could be readily effected by employing the highly useful expedient of masking the diene moiety as a 2-substituted 2,5-dihydrothiophene 1,1-dioxide (Scheme I). Thus, reaction of **5a** with the acid chloride **6**[5] (DMF, Et_3N, RT → 50 °C) afforded the latent enamido diene **7a**[9] (76%) which, upon brief heating in refluxing xylene pro-

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