As required, chemo- and stereoselective reaction at either the C-2 ($\alpha$-amino nitrile) or C-6 ($\alpha$-amino ether) centers of **3a** and **3b** could be achieved by an appropriate choice of reaction conditions. This is illustrated by the enantiospecific synthesis of both (+) and (−) enantiomers of coniine and dihydropinidine from these new synthons (Scheme II).

Alkylation of the anions of **3a** and **3b** with propyl bromide produced compounds **4a** and **4b** in nearly quantitative yields. Reaction of these products with $NaBH_4$ in EtOH (25–80 °C) then gave alcohols **5a** (9:1 mixture 2*S*:2*R* diastereomers, **5a** obtained pure by crystallization from hexane–EtOAc, 80%) and **5b** (98%). Under hydrogenolysis conditions the chiral auxiliary attached to the nitrogen of **5b** was cleaved giving (2*S*)-(+)-coniine (**6**)[10] [**6**·HCl, $[\alpha]^{20}_D$ +5.2° (EtOH, *c* 1.0)] in 95% yield (ee ≥ 98%).[11] More drastic conditions (70% $H_2SO_4$, Δ 15 h) were used to cleave the chiral side chain of **5a**; nevertheless excellent chemical and optical yields (94%, ee ≥ 98%) of (+)-coniine (**6**) were obtained.

The high stereoselectivity observed in the reactions of **4a** and **4b** with hydride ion implied a mechanism wherein there is prior formation of an iminium ion by elimination of the cyano group and subsequent approach of $H^-$ under complete stereoelectronic control[12] from the axial direction (upper face) to the iminium conformer **17**[13] (generating the 2*S* absolute configuration) (Scheme III).

By the same mechanism a propyl side chain was introduced at C-2 of **3a** in the opposite or *R* configuration on reaction with PrMgBr. For this transformation prior complexation of the cyano group with silver ion ($AgBF_4$, THF, 5 min → PrMgBr, 0 °C, 1 min) was necessary to ensure reaction of the amino nitrile moiety only. Compound **7a**, an 8:2 mixture of C-6 epimeric oxazolidines, was obtained in 25% yield after silica chromatography.[14] Reductive opening of the oxazolidine ring to **8a** ($NaBH_4$, EtOH) and cleavage of the chiral auxiliary by treatment with 70% $H_2SO_4$ then gave (*R*)-(−)-coniine (**9**) [**9**·HCl, $[\alpha]^{20}_D$ −5.80° (EtOH, *c* 1.0)] in high overall yield.

The key to the synthesis of (+)-dihydropinidine (**12**) from intermediates **4a** and **4b** involved the use of reaction conditions selective for the removal of the cyano group. This was accomplished by complexation of the cyano group with $AgBF_4$ followed by reaction with $Zn(BH_4)_2$ at low temperature (THF, −60 °C, 30 min). Compounds **10a** and **10b** (mixtures of oxazolidines with 2*S* configuration, 70–77%) were then reacted with $CH_3MgI$ ($Et_2O$, −60 °C, 20 h) giving the 2,6-*cis*-dialkylpiperidines **11a** (>95% cis, 87%) and **11b** (80:20 cis/trans, 70% after separation by column chromatography on silica). Hydrogenolysis of **11b** and treatment of **11a** with 70% $H_2SO_4$ led in each case to the formation of optically pure (2*S*,6*R*)-(+)-dihydropinidine (**12**) having the natural configuration [**12**·HCl, $[\alpha]^{20}_D$ +12.5° (EtOH, *c* 1.0)].[15]

In a similar fashion optically pure (−)-dihydropinidine (**16**) was prepared by selective reduction of **13b**, reaction of product **14b** with PrMgBr, and hydrogenolytic cleavage of the chiral auxiliary of **15b**.

In conclusion, reaction conditions were thus established that differentiated the reactivity of the amino nitrile and amino ether moieties of synthons **3a** and **3b** enabling the enantiospecific synthesis of (+)- and (−)-coniine and -dihydropinidine from a single starting material. Further applications of these versatile synthons to the asymmetric synthesis of more complex alkaloid systems are currently in progress.

**Acknowledgment.** We thank Dr. G. Cahiez for the $^{19}F$ NMR work and Drs. A. Schoofs and G. Lemoine for valuable discussions.

(10) Two chiral syntheses of (+)-coniine (**6**) have previously been reported: (a) Aketa, K. I.; Terashima, S.; Yamada, S. I. *Chem. Pharm. Bull.* **1976**, *24*, 621. (b) Archer, J. F.; Boyd, D. R.; Jackson, W. R.; Grundon, M. F.; Khan, W. A. *J. Chem. Soc. C* **1971**, 2560 (with an enantiomeric excess of 3–4%).

(11) The enantiomeric excesses were determined from a comparison of the $^{19}F$ NMR spectra of the "Mosher's" amide derivatives (Dale, J. A.; Dull, D. L.; Mosher, H. S.; *J. Org. Chem.* **1969**, *34*, 2543) of racemic coniine and the crude reaction products containing **6** and **9**. The signals for the $CF_3$ fluorines of the two enantiomers were separated by 0.78 ppm.

(12) Overman, L. E.; Freerks, R. L. *J. Org. Chem.* **1981**, *46*, 2833.

(13) Ring Inversion of **17** so as to reduce the $A^{1,2}$ interactions between the N-1–C-9 and C-6–O-7 bonds is prevented as the resultant conformer is highly strained (as determined from molecular models).

(14) Compound **7a** was present in the crude reaction mixture in approximately equal quantities with the enamine **2a** and the starting material **3a** (probably formed from **2a** by recapture of $CN^-$). Formation of **2a** indicates that deprotonation of the intermediate iminium ion by reaction with Grignard reagent competes with transfer of the propyl group.

(15) A chiral synthesis of (−)-dihydropinidine (unnatural enantiomer) has been previously achieved: Hill, R. K.; Yuri, T. *Tetrahedron* **1977**, *33*, 1569.

## Oxidation of Organic Compounds by Zinc Permanganate

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The reduction of permanganate ion to manganese dioxide in an aqueous medium liberates hydroxyl ions ($MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$). Potassium permanganate reaction mixtures therefore become alkaline as oxidation proceeds. This is not a problem with most substrates but, when the nature of the oxidation is pH dependent,[1] buffering of the medium may be necessary. Reagents employed for this purpose have included magnesium salts,[2] carbon dioxide,[3] and acetic acid.[4]

It was thought that magnesium permanganate and/or zinc permanganate should function as neutral oxidizing agents. Although a search of the literature revealed that this idea was not original,[5] magnesium permanganate and zinc permanganate appear to be virtually unknown as oxidizing agents in organic chemistry.[6]

These salts have now been prepared conveniently, by disproportionation of barium manganate[7] in water according to eq 1,

$$3BaMnO_4 + MO + 3H_2SO_4 \rightarrow M(MnO_4)_2 + MnO_2 + 3BaSO_4 + 3H_2O \quad (1)$$

in the presence of the stoichiometric amounts of sulfuric acid and magnesium oxide or zinc oxide, followed by filtration through Celite, evaporation of the filtrate, and crystallization from water. Both compounds are obtained as hexahydrates.

Astonishingly, both salts reacted instantly, with fires in some cases, when added to common laboratory solvents such as tetrahydrofuran, methanol, ethanol, *tert-butyl alcohol*, acetone, and *acetic acid*. By comparison, potassium permanganate was innocuous. These unexpected observations indicated that zinc permanganate and magnesium permanganate are powerful general oxidizing agents. Apparently complexation of zinc and magnesium cations to organic substrates greatly enhances their reactivity toward permanganate oxidation.

The oxidations of tetrahydrofuran and anisole were employed to determine whether a safe, general, experimental procedure could be developed. Oxidation in water solvent was inconvenient, because isolation of the product was laborious. A two-phase

(1) Wolfe, S.; Ingold, C. F.; Lemieux, R. U.; *J. Am. Chem. Soc.* **1981**, *103*, 938–939. Wolfe, S.; Ingold, C. F. *Ibid.* **1981**, *103*, 940–941.

(2) Wiberg, K. B.; Saegebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 2822–2824.

(3) Klein, E.; Rojahn, W. *Tetrahedron* **1965**, *21*, 2353–2358.

(4) Srinivasan, N. S.; Lee, D. G. *Synthesis* **1979**, 520–521.

(5) Powell, K. A.; Hughes, A. L.; Katchian, H.; Jerauld, J. F.; Sable, H. Z. *Tetrahedron* **1972**, *28*, 2019–2027.

(6) Chambliss, H. Ph.D. Dissertation, Johns Hopkins University, Baltimore, MD, 1900. We thank Professor G. H. Posner for a copy of this Thesis, which reports, inter alia, that magnesium permanganate ignites filter paper: Michael, A.; Garner, W. W. *Am. J. Chem.* **1905**, 267–271. Sable, H. Z.; Powell, K. A.; Katchian, H.; Niewoehner, C. B.; Kadlec, S. B. *Tetrahedron* **1970**, *26*, 1509–1524; Cornforth, J. W.; Cornforth, R. H.; Popjak, G.; Yengoyan, L. *J. Biol. Chem.* **1966**, *241*, 3970–3987.

(7) Lux, H. In "Handbook of Preparative Inorganic Chemistry"; Brauer, G., Ed.; Academic Press: New York, 1965; p 1462.

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Table I. Oxidation of Organic Compounds by Silica Gel Supported Permanganate Salts[a]

| entry | substrate | oxidant | oxidant/substrate[b] | temp, °C/solvent | time, h | product | yield, %[c] |
|---|---|---|---|---|---|---|---|
| 1 | PhC≡CPh | Zn[d] | 1.3 | 40/$CH_2Cl_2$ | 0.75 | PhCOCOPh | 67 |
| 2 | PhC≡CPh | Mg[e] | 1.3 | 40/$CH_2Cl_2$ | 24 | PhCOCOPh | 20 |
| 3 | PhC≡CPh | K[f] | 1.3 | 40/$CH_2Cl_2$ | 24 | PhCOCOPh | 0.5[g] |
| 4 | tetrahydrofuran | Zn | 2.0 | 20/$CH_2Cl_2$ | 0.25 | butyrolactone | 51[h] |
| 5 | tetrahydropyran | Zn | 2.0 | 20/$CH_2Cl_2$ | 0.17 | valerolactone | 69 |
| 6 |  | Zn | 2.0 | 60/$CHCl_3$ | 15 | PhCOPh | 88[i] |
| 7 |  | Zn | 2.0 | 60/$CHCl_3$ | 12 | $PhCOCH_3$ | 73[i] |
| 8 | cyclohexanone | Zn | 2.0 | 60/$CHCl_3$ | 15 | adipic acid | 69 |
| 9 | $PhCH_2NHBoc$ | Zn | 2.0 | 20/$CH_2Cl_2$ | 0.17 | PhCONHBoc | 72 |
| 10 |  | Zn | 2.0 | 60/$CHCl_3$ | 13 |  | 65 |
| 11 | $PhSCH_3$ | Zn | 1.2 | 20/$CH_2Cl_2$ | 2.5 | $PhSO_2CH_3$[j] | 92 |
| 12 |  | Zn | 1.5 | 20/$CH_2Cl_2$ | 3.5 |  | 36[l] |

[a] Prepared from the permanganate salt as described in ref 9; loadings determined iodometrically. Loadings ranging from 0.2 to 1.0 mM $MnO_4^-$/g of reagent give essentially the same conversions. [b] See text. [c] Isolated yield. Reactions have not been optimized. [d] $Zn(MnO_4)_2/SiO_2$. [e] $Mg(MnO_4)_2/SiO_2$. [f] $KMnO_4/SiO_2$. [g] 94% of the starting material was recovered. [h] Based on recovered THF, the conversion is 61%. [i] No deprotection was observed with silica gel alone under these conditions. [j] The reaction proceeds via the sulfoxide, which can be detected by TLC after short reaction times. [k] Ft = phthalimido. This new compound has mp 211–214 °C; IR (KBr) 3440, 1765, 1701 $cm^{-1}$; $^1$Hmr ($CDCl_3$) δ 7.86 (2 H, m), 7.77 (2 H, m), 5.04 (1 H, dd, 4, 11 Hz, C*H*OH), 4.20 (1 H, ddd, 4, 10, 14 Hz, C*H*Ft), 3.65 (1 H, d, 4 Hz, OH), 2.68 (3 H, m), 2.20 (1 H, m) 2.02 (1 H, m), 1.74 (1 H, m); EI-MS 259 ($M^+$); CI-MS 260 (M + 1). Anal. CHN. [l] This is the isolated yield; 33% of the starting olefin is recovered, and the products also include phthalimide (12%) and 2-phthalimidoadipic acid (8%).

water–methylene chloride oxidation was also unsuitable, because of the insolubility of the oxidizing agents in the organic phase. Addition of phase-transfer reagents[8] to this solvent system allowed oxidation to proceed, but as expected from the nature of phase transfer catalysis, the potassium, magnesium, and zinc salts gave virtually the same results. Analogous behavior was seen using the inorganic supports Celite, Florisil, and Linde 13X molecular sieves. It was then discovered that support on silica gel[9] preserved the rate enhancements associated with the zinc and magnesium cations, allowed a simple and general oxidation procedure to be developed, and provided oxidizing agents that could be handled safely,[10a] and employed under mild conditions.

Table I summarizes the results obtained from oxidations of a variety of monofunctional systems. Although most substrates were examined using each of the potassium, magnesium, and zinc salts, only one such comparison is given, in entries 1–3. The observations shown here are typical: the zinc salt is the most reactive, and the potassium salt is virtually unreactive under the same conditions.[11] The magnesium salt exhibits intermediate behavior. Addition of zinc sulfate or magnesium sulfate to supported potassium permanganate enhanced the reactivity of the latter, but the resulting reagent was not as effective as supported zinc permanganate or magnesium permanganate. Methylene chloride and chloroform were the best solvents for these oxidations, which could be performed either at room temperature or at reflux temperature, as necessary. The supernatant remains clear and colorless, and the workup consists of filtration and removal of the solvent.[12] For most of the examples shown, the resulting material contains only the product shown and unreacted substrate. In some cases, part of the product and/or unreacted starting material remains adsorbed on the support; elution in the normal manner increases the recoveries.

Although no attempt has been made to optimize specific oxidations, some general remarks can be made. The amount of oxidant shown in the oxidant/substrate column of Table I is based on the stoichiometry of the reaction indicated. For ratios between 1.0 and 2.0, the reactions do not proceed to completion because of precipitation of manganese dioxide on the surface of the supported permanganate. Four methods to overcome this problem have been examined: (A) use of excess permanganate; (B) slow addition of the solid oxidant to the substrate; (C) sonication of the reaction mixtures;[13] (D) filtration and addition of fresh oxidant once the initial reaction has ceased. Method D appears to afford the best results.

The following transformations are observed: acetylene → α-diketone (entry 1), cyclic ether → lactone (entries 4,5), cycloethylene ketal → ketone (entries 6,7), cyclic ketone → diacid (entry 8), acylated amine → acylimide (entries 9,10), sulfide →

(8) Foglia, T. A.; Barr, P. A.; Malloy, A. J. *J. Am. Oil Chem. Soc.* **1977**, *54*, 858A–861A. Lee, D. G.; Chang, V. S. *J. Org. Chem.* **1979**, *44*, 2726–2730.

(9) Regen, S. L.; Koteel, C. *J. Am. Chem. Soc.* **1977**, *99*, 3837–3838.

(10) (a) Under conditions of severe confinement and strong initiation, $KMnO_4$, $Mg(MnO_4)_2{\cdot}6H_2O$, and $Zn(MnO_4)_2{\cdot}6H_2O$ had energy releases 7%, 11%, and 13% that of trinitrotoluene. All tests of mechanical sensitivity and impact on the pure salts and the silica gel supported salts gave negative results.[10b] DTA and TGA measurements reveal no evidence of thermal instability of zinc and magnesium permanganate relative to potassium permanganate. (b) Personal communication from Dr. R. R. Vandebeek, Canadian Explosives Research Laboratory, Canada Centre for Mineral and Energy Technology, Ottawa.

(11) The lithium salt resembles the potassium salt in its oxidation behavior. For recent references to the sodium, silver, barium, and copper salts of permanganate, see: Menger, F. M.; Lee, C. *Tetrahedron Lett.* **1981**, *22*, 1655–1656. Firouzabadi, H.; Vessal, B.; Naderi, M. *Ibid.* **1982**, *23*, 1847–1850. Firouzabadi, H.; Mostafavipoor, Z. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 914–917. Lee, D. G.; Noureldin, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 3188–3191.

(12) For example: To a solution of phenyl methyl sulfide (310 mg, 2.5 mmol) in methylene chloride (50 mL) was added 17.4 g (4.00 mmol of permanganate) of zinc permanganate/$SiO_2$ (loading 0.23 mmol of permanganate/g of reagent). The mixture was stirred at room temperature for 2.5 h and filtered, the solid was washed with methylene chloride, and the combined filtrates were evaporated to give phenyl methyl sulfone, 354 mg (91%), mp 88–89 °C.

(13) We thank Professor D. J. L. Clive for this suggestion. See, e.g.: Han, B.-H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 5030–5032 and references cited. Yamawaki, W.; Sumi, S.; Ando, T.; Hanafusa, T. *Chem. Lett.* **1983**, 379–380.

sulfoxide → sulfone (entry 11), cyclic olefin → ketol (entry 12). Of these various transformations, only 6, 7, and 12 have not been observed previously. However, although each of the other oxidations shown in the table can be achieved in other ways, none of these has previously employed experimental conditions as simple or general as those reported here for oxidations by zinc permanganate.

With the completion of this preliminary survey of monofunctional organic substrates, the potential of zinc permanganate oxidation can now be applied to more complex polyfunctional molecules. The mechanisms of these reactions are also of interest; preliminary studies indicate that these mechanisms will differ in some respects from those observed for potassium permanganate oxidations in solution.

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**Registry No.** PhC≡CPh, 501-65-5; $PhCH_2NHBoc$, 42116-44-9; $PhSCH_3$, 100-68-5; PhCOCOPh, 134-81-6; PhCOPh, 119-61-9; $PhCOCH_3$, 98-86-2; PhCONHBoc, 88000-67-3; $PhSO_2CH_3$, 3112-85-4; $Zn(MnO_4)_2$, 23414-72-4; $Mg(MnO_4)_2$, 10377-62-5; $KMnO_4$, 7722-64-7; $BaMnO_4$, 7787-35-1; MgO, 1309-48-4; ZnO, 1314-13-2; tetrahydrofuran, 109-99-9; benzophenone ethylene ketal, 4359-34-6; acetophenone ethylene ketal, 3674-77-9; cyclohexanone, 108-94-1; *N*-phenylsulfonylpyrrolidine, 5033-22-7; tetrahydropyran, 142-68-7; butyrolactone, 96-48-0; valerolactone, 542-28-9; adipic acid, 124-04-9; *N*-phenylsulfonylpyrrolidin-2-one, 88000-68-4; 3-phthalimidocyclohexene, 1541-26-0; *trans*-2-hydroxy-3-phthalimidocyclohexanone, 88015-25-2.

## Tungsten-Catalyzed Allylic Alkylations. New Avenues for Selectivity

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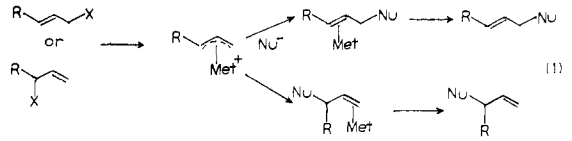
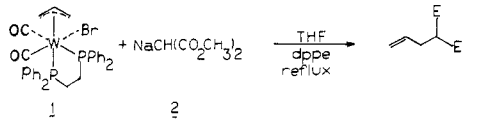
Transition-metal templates offer an opportunity to provide new dimensions for selectivity in organic reactions. In examining the question of regioselectivity of allylic alkylations,[1-4] we were intrigued by the possibility of enhanced selectivity for attack at the more substituted end of a $\pi$-allyl metal intermediate (eq 1). Five



(1)

factors may be envisioned to affect the regioselectivity—(1) steric demands of the nucleophile, (2) steric demands of the $\pi$-allyl substituents, (3) charge distribution of the $\pi$-allyl intermediate, (4) steric and electronic demands of the metal template, and (5) reactivity of the nucleophile. Rationalizing that factors 3 and 4 favor attack at the more substituted end, we envisioned that the steric demands imposed by a tungsten template may favor alkylation at the more substituted end. In this paper we wish to record (1) the development of a tungsten catalyst for allylic alkylation and (2) the unusual regio- and chemoselectivity of such alkylations.

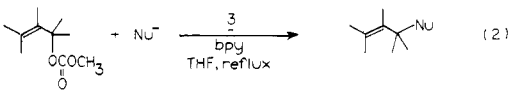
To establish the feasibility of nucleophilic attack on a $\pi$-allyltungsten complex,[5,6] we subjected **1**[5a,f] to dimethyl sodiomalonate (**2**) in refluxing THF; however, no alkylation occurred. On the other hand, addition of 1 equiv of dppe[7] to the refluxing mixture led to the alkylation product in 65% yield. We attribute the role



1 2

of the additional phosphine to ionization of **1**; the resultant cationic complex should be more susceptible to nucleophilic attack.

In order to develop a catalytic reaction, we used allyl acetate and **2** as the test reaction. We found that $W(CO)_6$ failed to catalyze the reaction[8] but that $(CH_3CN)_3W(CO)_3$[9] (**3**) led to a slow reaction (31% in 16 h). Addition of phosphines poisoned the catalyst. On the other hand, use of a stronger $\sigma$-donor type ligand such as bpy[7] to facilitate opening a coordination site on the tungsten led to a significant improvement (65% in 18 h). A more general reaction (see eq 2) resulted when carbonate, a slightly

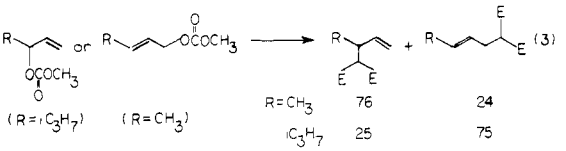


(2)

better leaving group than acetate, was substituted for acetate (81% in 12 h).

The allyl substrates that proved most interesting were those bearing one aryl group and are summarized in Table I. In each and every case, alkylation occurred predominantly to exclusively at the more substituted end regardless of the nucleophile. As expected, increasing the steric demands of the nucleophile did lead to some diminished regioselectivity (cf. entries 1, 4, and 5). Both electron-donating and electron-withdrawing aromatic rings succeed. In contrast to the molybdenum-catalyzed reactions,[2] sulfone-stabilized anions are good nucleophiles.

If both initial regioisomeric products are 1,2-disubstituted olefin–metal complexes, then a slightly diminished selectivity for the benzylic position occurs (entry 6). The effect of the aromatic ring on regioselectivity is discerned by comparing the results of the table to an alkyl-substituted $\pi$-allyl group as in eq 3. In the




(3)

latter cases steric demands of the nucleophile compete with the steric demands of the metal template to dominate the regioselectivity. Thus, the activation by the aryl group for displacement at a benzylic position conspires with the steric demands of the

(1) For reveiws, see: Trost, B. M. *Tetrahedron* **1977**, *33*, 2615; *Acc. Chem. Res.* **1980**, *13*, 385. Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 779. Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: Berlin, 1980.

(2) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543; **1983**, *105*, 3343.

(3) Roustan, J. L.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, 3721. Roustan, J. L.; Houlihan, F. *Can. J. Chem.* **1979**, *57*, 2790.

(4) Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1983**, *250*, C21.

(5) For their preparation, see: (a) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865. (b) Brisdon, B. J.; Cartwright, M.; Edwards, D. A.; Paddick, K. E. *Inorg. Chim. Acta* **1980**, *40*, 191. (c) Behrens, H.; Lindner, E.; Lehnert, G. *J. Organomet. Chem.* **1970**, *22*, 665. (d) Brisdon, B. J.; Edwards, D. A. *Ibid.* **1978**, *156*, 427. (e) Stiddard, M. H. B.; Hull, C. G. *Ibid.* **1967**, *9*, 519. (f) Brisdon, B. J. *Ibid.* **1977**, *125*, 225. (g) Brisdon, B. J.; Griffin, G. F. *Ibid.* **1974**, *76*, C47. (h) Dawans, F.; Dervailly, J.; Meirnier-Piret, J.; Piret, P. *Ibid.* **1974**, *76*, 53. (i) Stiddard, M. H. B.; Holloway, C. E.; Kelly, J. D. *J. Chem. Soc. A* **1969**, 931. (j) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588, 3183.

(6) For a report of attack by hydride and Grignard reagents on a bis(cyclopentadienyl)-$\pi$-allyltungsten complex, see: Green, M. L. H.; Ephritikhine, M.; Francis, B. R.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc. Dalton Trans.* **1977**, 1131.

(7) Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane, bpy = 2,2'-bipyridyl, E = $CO_2CH_3$.

(8) For a stoichiometric reaction of allyl trifluoroacetate and $W(CO)_6$, see ref 5h.

(9) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865 and references cited therein.

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