material, prepared[11] from (20*R*)-3β-hydroxy-5-cholenic acid (**6**)[12] showed no depression. As further proof, hydrogenation of triene **3** with palladium on carbon in ethanol yielded hexahydro ester **7**[9] (97%), mp 159–160 °C (lit.[10] 159–160 °C). The spectral data from this compound were also identical with those previously reported,[10] and the melting point of a mixture of **7** and authentic material prepared by hydrogenation of the natural cholenic acid derivative **5** showed no depression. These data prove conclusively that the *R* configuration assigned at C-20 is correct.

The corresponding 3β-hydroxy compound (**2**) afforded the analogous ene product (**4**), stereospecifically in 95% yield. Although this material did not exhibit a sharp melting point (80–90 °C) after repeated recrystallizations (due perhaps to polymorphism or hygroscopic tendencies), its spectral data supports the proposed structure. In addition, treatment of **4** with acetic anhydride at reflux for 2 h produced material in 85% yield which was identical with triene **3**, and a melting point of a mixture of these products exhibited no depression.

The same reaction conditions were employed to convert the ethylidene derivative of estrone methyl ether **8**[6] via the ene reaction to ester **9**[9] (90%): mp 83–84 °C; IR ($CHCl_3$) 1710, 1650, 1610, 1020, and 980 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (d, 3, J = 8 Hz, 21-H), 5.40 (dd, 1), 5.80 (dd, 1, J = 1.5, 16 Hz), 6.90 (dd, 1, J = 8, 16 Hz).

Of all the published procedures,[1,2] this process is the most direct and highest yielding stereospecific method for the attachment of a steroidal side chain and is the only process which has been reported to proceed directly on an unprotected, unsaturated steroidal alcohol.

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(11) Wallis, E. S.; Fernholz, E. *J. Am. Chem. Soc.* **1935**, *57*, 1504.

(12) This material was generously supplied by Dr. M. Tanabe, Stanford Research Institute.

Alkylidene Complexes from the Reactions of Transition-Metal Dianions with Iminium Salts: Synthesis and Spectral Characterization of $[Mo(CO)_5CPh_2]$

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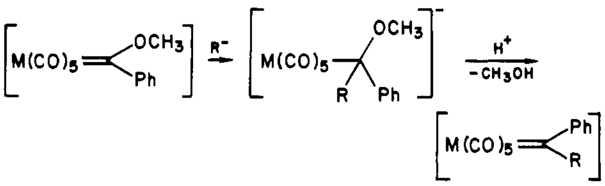
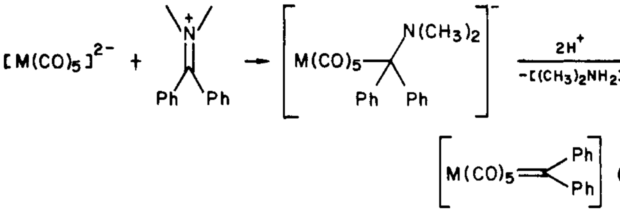
Important recent developments in the chemistry of the transition metal to carbon double bond have included syntheses of alkylidene complexes, in a variety of metal–ligand environments, lacking the stabilizing heteroatomic substituents characteristic of the carbene complexes prepared by Fischer and others.[1-3] A notable early example of such a complex was $[W(CO)_5CPh_2]$,[1c] prepared from an alkoxycarbene complex as shown in eq 1 (R = Ph). Subsequent studies of the reactions of this species with alkenes[4] have had an important influence on the development of current ideas about the mechanism of the alkene metathesis reaction and focused considerable attention on the chemistry of this and related species. Fischer has reported independent syntheses of related W and Cr complexes[1f] and the successful isolation of one of the intermediate tungstates,[1g] and Casey has also prepared thermally unstable monoarylalkylidenes in this metal–ligand environment (eq 1, R = H, Me).[1d,e]



(1)

We wish to report the synthesis and characterization of a new alkylidene complex, $[Mo(CO)_5CPh_2]$, which, together with the species $[M(CO)_5CPh_2]$ (M = Cr, W), provides the first example of the isolation of a set of isologous alkylidene complexes containing each of the metals of a d-block triad. The preparation of the complex (eq 2, M = Mo) involves nucleophilic attack of a transition-metal dianion on an imminium salt to give an (aminomethyl)metalate, closely related to the (alkoxymethyl)metalate in eq 1, which can be deaminated to give the alkylidene. We have demonstrated the potential of sequences of this type as general routes to alkylidene complexes by preparing the Cr and W analogues of the Mo complex in a similar manner (eq 2, M = Cr, W).



(2)

Addition of 3.38 mmol of powdered $[Ph_2CNMe_2][OSO_2F]$[5] to a solution of 3.52 mmol[6] of $Na_2[Mo(CO)_5]$ in 25 mL of tetrahydrofuran (THF)[7] at −78 °C resulted in a smooth reaction to give, after 1 h, a red-purple solution containing only traces of suspended solid. The solution changed color to light amber after addition of 28.3 mmol of CF_3CO_2H at −78 °C and was then warmed to −35 °C. At this temperature a slow reaction occurred to give, after 3 h, an intensely colored red solution containing the product alkylidene complex. Excess acid was neutralized by

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(1) For alkylidene syntheses, see: (a) Öfele, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 950. (b) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430. (c) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *Ibid.* **1977**, *99*, 2127. (d) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282. (e) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *Ibid.* **1977**, *99*, 2533. (f) Fischer, E. O.; Held, W.; Kreissl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656. (g) Fischer, E. O.; Held, W.; Kreissl, F. R. *Ibid.* **1977**, *110*, 3842. (h) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (i) Fischer, E. O.; Clough, R. L.; Besl, G.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543. (j) Fischer, E. O.; Clough, R. L.; Stuckler, P. *J. Organomet. Chem.* **1976**, *120*, C6. (k) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98 and references therein.

(2) We adhere to the convention[1k] of referring to complexes with α-heteroatomic substituents as carbene complexes and those lacking such substituents as alkylidene complexes.

(3) For reviews of carbene complexes, see: (a) Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353. (b) *Ibid.* **1970**, *24*, 407. (c) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (d) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99. (e) Fischer, E. O. *Pure Appl. Chem.* **1978**, *50*, 857. (f) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487.

(4) (a) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808. (b) Katz, T. J.; McGinnis, J.; Altus, C. *Ibid.* **1976**, *98*, 606. (c) McGinnis, J.; Katz, T. J. Hurwitz, S. *Ibid.* **1976**, *98*, 605.

(5) Readily prepared by condensing benzophenone with methylamine to form Ph_2CNMe and methylating this imine with $MeOSO_2F$ in CH_2Cl_2: Tennant, G. In "Comprehensive Organic Chemistry"; Sutherland, I. O., Ed.; Pergamon Press: Elmsford, NY, 1979; Vol. 2, p 385.

(6) Based on the quantity of amine complex used to prepare the dianion.[7]

(7) $Na_2[W(CO)_5]$,[8] $Na_2[Mo(CO)_5]$,[8] $Na_2[Cr(CO)_5]$,[9] and $Li_2[W(CO)_5]$ can be obtained in high yield and purity as THF solutions by reduction of $[M(CO)_5(NMe_3)]$ (M = Cr, Mo, W) with the appropriate alkali naphthalide. Details of the preparation of these and other transition-metal dianions will be published shortly: Maher, J. M.; Beatty, R. P.; Cooper, N. J., manuscript in preparation.

(8) (a) Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357. (b) Ellis, J. E.; Hagen, G. P. *J. Am. Chem. Soc.* **1974**, *96*, 7525.

(9) Ellis, J. E.; Hentges, S.; Kalina, D.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79.

stirring the solution for 45 min at −78 °C with 0.11 mol of powdered Na_2CO_3 which had been flame-dried under vacuum, and the solvent was removed from the filtered solution at −35 °C under vacuum. The resulting gummy solid was extracted with 150 mL of 2:1 pentane:diethyl ether in three aliquots, and the solvent was removed under vacuum at −35 °C. The product was recrystallized from 10 mL of pentane at −80 °C to give dark red crystals.

The ^{13}C and ^1H NMR spectra[10] of the compound showed that it was $[Mo(CO)_5CPh_2]$.[11] The ^{13}C NMR spectrum was particularly informative, showing resonances which could be attributed to the alkylidene carbon, the trans carbonyl ligand, the four equivalent cis carbonyl ligands, and the carbons of the phenyl groups at frequencies very similar to those reported for the Cr and W analogues.[1f] The visible spectrum of the compound[12] is very similar to that of the W analogue, and we were able to use the extinction coefficient of the main absorption at 503 nm to determine that crude mixtures contained ca. 25% yields[13] of the product. The isolated yield[13] of the product was 15%. The molybdenum complex is considerably less stable thermally than its Cr and W analogues, with a half-life of approximately 2 h at −20 °C in toluene.[14] The complex is also air and light sensitive.

No observable reaction occurred when $[Mo(CO)_5CPh_2]$ was dissolved in isobutylene at temperatures below −10 °C, but at room temperature decomposition to $[Mo(CO)_6]$[15] and a mixture of organic products was complete in 2 h. The diphenylalkylidene moieties were recovered in three forms:[16] 40% as 1,1-diphenylethylene, 45% as 1,1,2,2-tetraphenylethane, and 15% as hexaphenylcyclopropane. The formation of 1,1-diphenylethylene indicates that a metathetical reaction is occurring analogous to that observed when $[W(CO)_5CPh_2]$ is heated in isobutylene, but the isolation of a similar quantity of 1,1,2,2-tetraphenylethane[17] would suggest that this reaction is competitive with thermal decomposition of the complex.

The complexes $[Cr(CO)_5CPh_2]$ and $[W(CO)_5CPh_2]$ were also prepared by the reaction sequence outlined in eq 2, with only minor variations in the experimental details. In the Cr case, the deamination of the intermediate metalate was carried out at −30 °C, and the solvent could be removed from the crude product at −15 °C. Pentane solutions were handled at −5 °C, and pure $[Cr(CO)_5CPh_2]$[19] was finally obtained in 53% yield. In the W case, the deamination was carried out at 0 °C, and the material could be handled in solution at 0 °C. The yield of recrystallized $[W(CO)_5CPh_2]$[20] was 27%.

The low yields of the tungsten and molybdenum complexes prompted extensive experiments to determine the optimum conditions for the tungsten reaction. Deamination with other proton acids or with Lewis acids gave poorer results, and the quantity of excess acid used in deamination did not have a significant influence on the reaction. Varying the temperature at which the initial reaction between the dianion and the imminium salt was carried out from −78 to −40 °C had no effect on the yield, nor did the use of $Li_2[W(CO)_5]$[7] or $Cs_2[W(CO)_5]$.[9]

Chromatographic investigation of the organic side products formed in the tungsten reaction resulted in the isolation of a 30% yield of Ph_2CHNMe_2[16] and traces of benzophenone. The two side reactions most likely to give rise to this amine are one-electron transfer during the reaction of the dianion with the imminium salt to give $Ph_2CNMe_2\cdot$, which could abstract H· from the solvent, from the solvent, or alternatively protonation at the metal which could be followed by reductive elimination to give the amine during the deamination. Use of DCl in ether for the deamination gave a 3:1 mixture of the d_0 and d_1 Ph_2CHNMe_2, and since control experiments showed that the amine was stable to exchange under the isolation conditions, it was concluded that both side reactions were occurring but that one-electron transfer was the major competing reaction.

No direct evidence was obtained for the formation of the putative intermediate (aminomethyl)metalates during these reactions. Several attempts were made to isolate the product of the initial reaction between $Na_2[W(CO)_5]$ and $[Ph_2CNMe_2][OSO_2F]$ by using methods analogous to those which enabled Fischer and his co-workers to characterize the closely related species $[N(PPh_3)_2][W(CO)_5C(OMe)Ph_2]$,[1g] but no tractable complexes were obtained. Precedent does, however, exist for nucleophilic attack by transition-metal anions on iminium salts in the reaction of $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$ with iminium salts to give species of the type $[Fe(\eta\text{-}C_5H_5)(CO)_2CR_2NR'_2]$[21] and the preparation of Fe- and Cr-aminocarbene complexes from reactions of dianionic precursors with a chloroformiminium chloride,[22] a chloroformamidinium chloride,[22] and dimethylformiminium iodide.[23]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Exxon Educational Foundation, and the National Science Foundation (Grants CHE78-25699 and CHE80-16162) for financial support.

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[10] $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2, −40 °C) 384.2 (s, CPh_2), 223.5 (s, *trans*-CO), 206.0 (s, *cis*-CO), 163.9, 131.1, 127.4, 126.0 (C_6H_5). ^1H NMR (δ, CD_2Cl_2, −40 °C) 7–8 (m, C_6H_5). These spectra showed that $Mo(CO)_6$ and pentane were trace impurities.

[11] The instability of the product precluded elemental analysis.

[12] Visible spectrum (pentane, −35 °C) 423 (sh), 503 nm (ϵ 10 000).

[13] Based on the quantity of iminium salt used in the reaction.

[14] $t_{1/2}$ = 11 h for $[W(CO)_5CPh_2]$ in pentane at 30 °C: Fong, L.; Cooper, N. J., unpublished results.

[15] As indicated by IR spectra of the solution.

[16] Characterized by ^1H NMR and MS.

[17] This could be formed from diphenylcarbene, or a related carbenoid, by an abstraction–recombination sequence involving the solvent.[18]

[18] Kirmse, W.; Horner, L.; Hoffmann, H. *Liebigs Ann. Chem.* **1958**, *614*, 19.

[19] Identified by comparison of its ^{13}C NMR spectrum with that reported in the literature.[1f]

[20] Identified by comparison of IR, ^1H NMR, and UV/visible spectra of the solution with those of an authentic sample.[1c]

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[23] Fong, C. W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100.

A Mild Procedure for the Generation of Azomethine Imines. Stereochemical Factors in the Intramolecular 1,3-Dipolar Addition of Azomethine Imines and a Synthetic Approach to Saxitoxin

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Saxitoxin (**4**), the paralytic agent of the California mussel *Mytilus californianus*,[1] has long been recognized as one of the most toxic of the nonprotein poisons known. With an LD_{50} in mice of 5–10 μg/kg, it has been suggested that a single dose of 0.2–1.0 mg would prove fatal in humans. Paradoxically, however, this identical substance is also the object of intense medical interest,[5] and as a consequence the synthesis of this molecule continues to be an intriguing and important goal.[4]

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† On leave from Boehringer Ingelheim Ltd., July–Nov, 1978.

[1] For the comprehensive listing of sources for the isolation of saxitoxin, see V. E. Ghazarossian, E. J. Schantz, H. K. Schnoes, and F. M. Strong, *Biochem. Biophys. Res. Commun.*, **59**, 1219 (1974). Other noteworthy studies include the structural work of Rapoport,[2] the X-ray analysis by Clardy and Schantz,[3] and the elegant total synthesis by Kishi et al.[4]

[2] J. L. Wong, R. Oesterlin, and H. Rapoport, *J. Am. Chem. Soc.*, **93**, 7344 (1971), and references cited therein. See also J. Bordner, W. E. Thiessen, H. A. Bates, and H. Rapoport, *J. Am. Chem. Soc.*, **97**, 6008 (1975).

[3] E. J. Schantz, V. E. Ghazarossian, H. K. Schnoes, F. M. Strong, J. P. Springer, J. O. Pezzanite, and J. S. Clardy, *J. Am. Chem. Soc.*, **97**, 1238 (1975).

[4] H. Tanino, T. Nakata, T. Kaneko, and Y. Kishi, *J. Am. Chem. Soc.*, **99**, 2818 (1977).

[5] B. H. Takman, R. N. Boyes, and H. G. Vassallo in "Principles of Medicinal Chemistry", W. O. Foye, Ed., Lea and Febiger, Philadelphia, 1974, p 316. See also J. M. Ritchie and R. B. Rogart, *Rev. Physiol. Biochem. Pharmacol.*, **79**, 1 (1977); *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 211 (1977).

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