carbon bond-forming reactions are of considerable general importance to organic synthesis.[31] The present reaction affords the addition product 4 in good yield and without accompanying side processes. Cycloaddition of TCNE to coordinated allyl, observed for $(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl$,[4] does not occur here. The use of bis(allyl)metal complexes in the development of these and related co-oligomerization reactions, and mechanistic studies of such processes, are under continuing investigation.

Acknowledgment. We wish to acknowledge financial support of this investigation by NATO (Grant No. 068.81), the Ministero Pubblica Istruzione (Rome), and the National Science Foundation (Grant CHE-7911882).

Registry No. **1a**, 75110-81-5; **1b**, 75110-82-6; **2**, 98689-94-2; **3**, 98689-95-3; **4**, 98704-14-4; **5**, 98689-96-4; **6**, 98689-97-5; TCNE, 670-54-2; PPh_3, 603-35-0; Pt, 7440-06-4; 3,3,4,4-tetracyanobicyclo[4.2.0]octane, 98704-15-5.

(31) See, for example: Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 14.

Chromium Tricarbonyl Complexes of Estradiol Derivatives: Differentiation of α- and β-Diastereoisomers Using One- and Two-Dimensional NMR Spectroscopy at 500 MHz

Siden Top,[†] Gérard Jaouen,*[†] Anne Vessières,[†] Jean-Pierre Abjean,[†] Daniel Davoust,[‡] Charles A. Rodger,[§] Brian G. Sayer,[⊥] and Michael J. McGlinchey*[⊥]

Ecole Nationale Supérieure de Chimie, 75231 Paris Cedex 05, France, Université de Paris VI, 75230 Paris Cedex 05, France, Bruker Spectrospin Ltd., Milton, Ontario L9T 1Y6, Canada, and Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Received May 24, 1985

The steroidal hormone β-estradiol and its derivatives in which the hydroxyl functionalities have been protected by benzyl or dimethyl-*tert*-butylsilyl groups bond to a tricarbonylchromium moiety via either the α- or the β-face of the arene ring. Unambiguous differentiation of these diastereomers is difficult without recourse to X-ray crystallographic techniques. These molecules have been characterized by 500-MHz ^1H and 125-MHz ^{13}C NMR spectroscopy; assignments are made by using the two-dimensional techniques COSY and SECSY as well as heteronuclear shift-correlated spectra. Thus, high field NMR spectroscopy provides a straightforward method of differentiating between the α- and β-isomers.

Introduction

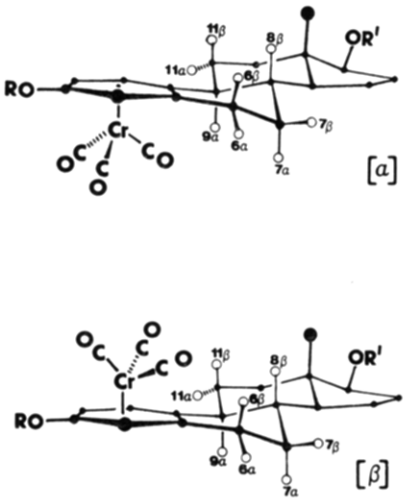
The biochemical importance of steroidal hormones which have been modified by the incorporation of organometallic moieties has only recently been appreciated. These species can function as markers in the study of receptors;[1] they are useful in immunology[2] and also serve as synthetic intermediates in regio- and stereospecific functionalizations.[3] It is of course well documented that such organometallic complexes are of great synthetic utility, but they also show promise of unprecedented applications in the field of molecular biology.[1] This promise is founded first on the ability of metal carbonyl derivatives of hormones to recognize their specific receptor and secondly on the strong absorptions of the carbonyl ligands in the infrared region 2100–1850 cm^{-1}; this frequency range is compatible with a window in which the proteins do not absorb. This concept opens new vistas whose full potential can hardly be ascertained at present. We note that this extension beyond the normal realm of transition-metal complexes and into bioorganometallic chemistry has only become viable with the advent of Fourier transform infrared techniques which lowers the threshold of detection of so labeled hormones to the level of a few femtomoles per milligram of protein.[1] This concentration corresponds to that commonly encountered in biological systems and so could be used to monitor the hormone dependence of breast cancer. Nevertheless, in spite of this enormous potential, there are still very few studies reported on these complexes.[4] In particular, the complexation of the arene ring of estradiol and its derivatives with a tripodal group, such as $Cr(CO)_3$, is a diastereogenic reaction. The organometallic moiety can bind either to the "α" or to the "β" face of the hormone, as shown below.

The structure of the free hormone has been established by X-ray techniques[5] but there are presently insufficient data to allow unambiguous structural assignments of or-

[†] Ecole Nationale Supérieure de Chimie.
[‡] Université de Paris VI.
[§] Bruker Spectrospin Ltd.
[⊥] McMaster University.

(1) Jaouen, G.; Vessières, A.; Top, S.; Ismail, A. A.; Butler, I. S. *J. Am. Chem. Soc.* **1985**, *107*, 4778.
(2) Cais, M. *Actual. Chim.* **1979**, *7*, 14.
(3) (a) Jaouen, G.; Top, S.; Laconi, A.; Couturier, D.; Brochard, J. *J. Am. Chem. Soc.* **1984**, *106*, 2207. (b) Top, S.; Vessières, A.; Abjean, J.-P.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1984**, 428.
(4) (a) Pouskouleli, G.; Butler, I. S.; Hickey, J. P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1659: in this work the diastereomers were not cleanly separated and some of the stereochemical assignments need to be reassessed. (b) Hickey, J. P.; Butler, I. S.; Pouskouleli, G. *J. Magn. Reson.* **1980**, *38*, 501. (c) Birch, A. J.; Cross, P. E.; Connor, D. T.; Subba Rao, G. S. R. *J. Chem. Soc. C* **1966**, 54. (d) Howsam, R. W.; McQuillin, F. J. *Tetrahedron Lett.* **1968**, 3667. (e) Henderson, K.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1978**, 15. (f) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743. (g) Shimuzu, Y.; Mitsuhashi, H.; Caspi, E. *Tetrahedron Lett.* **1966**, 4113.
(5) (a) Busetta, B.; Hospital, M. *Acta Crystallog., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 560. (b) Busetta, B.; Courseille, C.; Geoffre, S.; Hospital, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1349. (c) Duax, W. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1864.

0276-7333/85/2304-2143$01.50/0



ganometallic derivatives without recourse to crystallography; however, it would be inconvenient to have to adopt this approach for every diastereomer and so we have sought other analytical techniques which might alleviate this problem.

This paper describes the determination of the configurations of a series of organometallic derivatives of estradiol. Commonly used physico chemical techniques such as infrared spectroscopy, optical rotation ($|\alpha|_D$), and chromatographic retention indices (R_f values) are discussed; it is proposed that high field NMR spectroscopy provides an unequivocal criterion for the establishment of the site of complexation by the organometallic moiety.

Results and Discussion

Synthetic Aspects. The most straightforward way to mark estra-1,3,5(10)-triene-3,17β-diol, **1**, is to take advantage of the presence of the aromatic ring in the steroid. The attachment of a 12-electron moiety, such as $Cr(CO)_3$, can occur on either the α- or the β- face of the chiral hormone. By virtue of the dissymmetric substitution pattern in the A ring, this complexation generates planar chirality[6] and so a diastereomeric mixture results. For the synthetic and biochemical applications, it is of pivotal importance to establish the exact site of complexation in this series of molecules. Perhaps the most definitive technique is X-ray crystallography; hence the absolute configuration of one molecule in this series has been determined[7] and the others assigned via appropriate chemical correlations. The synthetic results are summarized in Scheme I and show that reaction of 17β-estradiol with $Cr(CO)_6$ yields a diastereomeric mixture of **2** and **3**. Protection of the phenolic groups by incorporation of benzyl functionalities led to a diastereomeric mixture of **4** and **5**. Following chromatographic separation of this mixture, each diastereomer was treated with sodium hydride in tetrahydrofuran and subsequently with *tert*-butyldimethylchlorosilane to give the doubly protected estradiol complexes **6** and **7**. The free doubly protected estradiol **8** is obtainable by simple photolysis in sunlight. Alternatively, one can silylate the phenolic substituent in **1** before complexation to give **9**; subsequent reaction with hexacarbonylchromium(0) yields a diastereomeric mixture of **10** and **11** which may also be separated chromatographically. These latter two $Cr(CO)_3$ complexes can be converted into their corresponding dicarbonyl thiocarbonyl analogues, **12** and **13**, upon irradiation and reaction with CS_2. The monosilylated complexes **10** and **11** can be further silylated at the 17-position to give **14** and **15**; again the $Cr(CO)_3$ moiety is removable photolytically to yield the doubly silylated estradiol **16**.

Scheme I

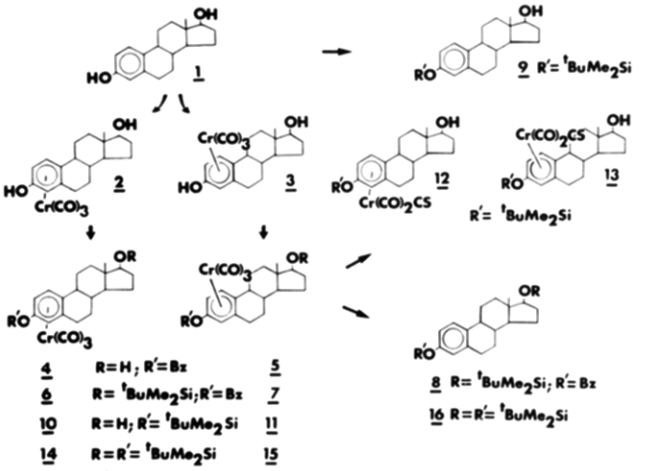


Table I. Optical Rotations of Molecules 1–16[a]

	2[b]	4[c]	6[c]	10[d]	12[d]	14[c]
α-series	+45.0°	+28.5°	+35.0°	+38.7°	+20.8°	+36.5°
	3[b]	**5**	**7**[c]	**11**[d]	**13**[d]	**15**[c]
β-series	+54.3°	+84.0°	+53.3°	+62.5°	+17.7°	+45.3°

[a] The $|\alpha|^{21}_D$ values in the table are for α/β pairs of Cr complexes; values for the free ligands are as follows: **1**, 80.4° (dioxane); **8**, 39.6° ($CHCl_3$); **9**, 58.5° (CH_2Cl_2); **16**, 43.1° (CH_2Cl_2). [b] In acetone. [c] In $CHCl_3$. [d] In CH_2Cl_2.

Establishment of the Absolute Configurations of the Complexes. In order to establish unequivocally the structure of one complex, it was found that the most satisfactory crystals were those of the thiocarbonyl complex **12**; X-ray crystallographic determination[7] of the structure revealed that the (thiocarbonyl)dicarbonylchromium tripod is attached to the α-face of the steroid as depicted in Scheme I. This immediately identifies **10** (the precursor of **12**) as the α-isomer; since **14** is merely the product obtained by a second silylation of **10**, this complex must have the same α-configuration. The chemical correlation between the benzylated and the silylated series of complexes was made by taking one of the nonprotected (estradiol)$Cr(CO)_3$ complexes, **2**, and treating it with NaH and *t*-$BuMe_2SiCl$ to give **10**; subsequent photolysis and reaction with CS_2 yielded a compound identical in all respects with **12**. Furthermore, benzylation of **2** gave the complex **4** and established all of these molecules as possessing α-$Cr(CO)_3$ groups. Thus, the molecules numbered **3**, **5**, **7**, **11**, **13**, and **15** must be the β-isomers.

Having established the absolute configurations of the molecules **2** through **15**, one can now examine the analytical methods available which, in principle, might be used to provide a relatively simple yet definitive means of differentiating between α- and β-complexes. At first sight, one might have visualized that the β-complexed molecules should be sterically disfavored because of nonbonded interactions between the tripod and the methyl group at C-13; indeed, the behavior of the $Cr(CO)_3$ complexes of the methylindans supports this idea.[8] However, the relative

(6) Jaouen, G. In "Transition Metals in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, pp 65–120.

(7) (a) Louër, M., manuscript in preparation. (b) The (estradiol)$Cr(CO)_3$ derivatives are described as α- and β-diastereomers depending on the location of the tripod on the α- or β-face of the hormone.

(8) Gracey, D. E. F.; Jackson, W. R.; Jennings, W. B.; Rennison, S. C.; Spratt, R. *J. Chem. Soc. B* **1969**, 1210.

yields of α- to β-isomers do not reflect the supposed importance of this steric effect. Thus, the experimental data (56:44 for **4**:**5** and 41:59 for **10**:**11**) reveal that the proportions of the diastereomers are inverted when one passes from one series to the other. Clearly, one cannot use such a criterion in these cases since it is difficult to know whether the reaction is thermodynamically or kinetically controlled. Furthermore, the incorporation of substituents which may interact competitively make predictions difficult. Thus, 1-methylindan leads preferentially to the exo isomer (presumably for steric reasons); in contrast, 1-indanol yields exclusively the endo configuration.[6,8] In estradiol, however, these same two substituents are positioned contiguously on the β-face and the relative importance of these opposing effects is unpredictable.

The specific rotation, $|\alpha|_D$, is often used as a guide to the molecular configuration. Although, as shown in Table I, the β-isomers generally exhibit the larger rotation, the thiocarbonyl complexes **12** and **13** are anomalous and demonstrate the inherent problems with this approach. The R_f values on silica gel plates are larger for the α-isomers than for the corresponding β-isomers for all the complexes studied herein. This may be a reflection of the relative polarities of the α- and β-isomers, but one must be prudent in view of the small number of complexes currently known.

The infrared stretching frequencies of the carbonyl functionalities have been used to probe the hormone–receptor binding.[1] However, in the complexes studied, the IR method does not permit the determination of the absolute configurations as all ν_{CO} values are identical for pairs of diastereomers.

High-Resolution ^{1}H and ^{13}C NMR Spectroscopy. The advent of high field NMR spectrometers has opened new vistas to those who seek to determine the structures of complex molecules in solution. Spin decoupling and nuclear Overhauser effects have become familiar tools for making connections between nuclei through bonds and through space, respectively. However, there have been major limitations on the use of these techniques; both the irradiated and observed resonances need to be sufficiently well resolved to allow the experiment to be carried out and interpreted.

Recently, Hall and Sanders undertook an exhaustive study of a steroidal system using NOE and spin decoupling difference spectroscopy at a high field where the problem of overlapping resonances in the ^{1}H NMR spectrum may be largely avoided.[9] However, despite the spectral dispersion achieved at a magnetic field of 9.4 T (400-MHz ^{1}H resonance frequency), simple "old-fashioned" one-dimensional experiments may still yield ambiguous results. Figure 1 shows the partial proton spectrum of 3-(benzyloxy)-17β-(*tert*-butyldimethylsiloxy)estra-1,3,5(10)-triene, **8**, obtained at 500 MHz. Clearly, despite the chemical shift dispersion achievable at such a high magnetic field, overlapping resonances preclude the use of traditional assignment techniques.

The strategy adopted in this study of estradiol complexes utilizes some recently developed multipulse NMR techniques to assign unambiguously each proton and carbon. COSY and SECSY are two-dimensional experiments which allow molecular structure elucidation through scalar coupling between protons.[10] Figure 2 shows the result of a COSY experiment presented here as a contour plot in which a coupling between two spins is manifested as a pair of off-diagonal peaks. Careful scrutiny of the 2-D matrix allows assignment of the framework of the estradiol molecule despite the complexity of the normal one-dimensional spectrum. Typically, the resonance centered at 2.32 ppm assigned as the H-9 proton clearly shows scalar coupling correlations to the methine H-8 proton and to the

Table II. ^{1}H NMR Chemical Shifts (ppm)

hydrogen	free arene **8**	α-complex **6**	β-complex **7**
1	7.44	5.60	5.42
2	7.11	4.95	4.75
4	7.04	4.90	4.89
6α	2.96	2.76	2.44
6β	2.99	2.56	3.01
7α	1.44	1.61	1.11
7β	1.96	1.72	1.90
8	1.57	1.17	1.80
9	2.32	2.15	1.85
11α	2.41	1.93	1.97
11β	1.70	1.27	1.95
12α	1.31	1.05	1.19
12β	2.12	1.91	2.12
14	1.12	0.70	0.95
15α	1.72	1.54	1.60
15β	1.44	1.31	1.40
16α	2.07	2.04	2.02
16β	1.74	1.72	1.72
17	3.74	3.65	3.74
18	1.03	0.93	1.15
Me_2[a]	0.34/0.32	0.37/0.35	0.34/0.32
t-Bu	1.25	1.27	1.26

[a] These methyl groups are diastereotopic.

Table III. Geminal and Vicinal Coupling Constants in Rings B and C

		$\|^3J\|$, Hz		
proton pair	$\|^2J\|$, Hz	ax–ax	ax–eq	eq–eq
6α,6β	16.9			
6α,7α			5.9	
6α,7β				1.6
6β,7α		12.8		
6β,7β			6.4	
7α,7β	12.2			
7α,8β		11.1		
7β,8β			2.6	
8β,9α		11.1		
8β,14α		11.1		
9α,11α			3.8	
9α,11β		12.0		
11α,11β	13.2			
11α,12α			4.0	
11α,12β				3.1
11β,12α		12.7		
11β,12β			3.9	
12α,12β	12.5			

Table IV. Geminal and Vicinal Coupling Constants in Ring D (in Hz)

proton	14α	15β	16α	16β	17α
15α	6.7	12.4	9.5	3.2	
15β	12.3		5.9	12.4	
16α		5.9		13.1	8.7
16β		12.4	13.1		8.0

(9) (a) Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703. (b) Hall, L. D.; Sanders, J. K. M. *J. Org. Chem.* **1981**, *46*, 1132. (c) Sanders, J. K. M.; Mersh, J. D. *Prog. NMR Spectrosc.* **1982**, *15*, 353.

(10) (a) Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350. (b) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *42*, 164. (c) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542. (d) Freeman, R.; Morris, G. A. *Bull. Magn. Reson.* **1979**, *1*, 5. (e) Nagayama, K.; Kumar, A.; Wüthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321. (f) Hull, W. E. "Two-Dimensional NMR"; Bruker Analytische Messtechnik: Karlsruhe, 1982: this brochure contains much valuable experimental information as well as a literature survey.

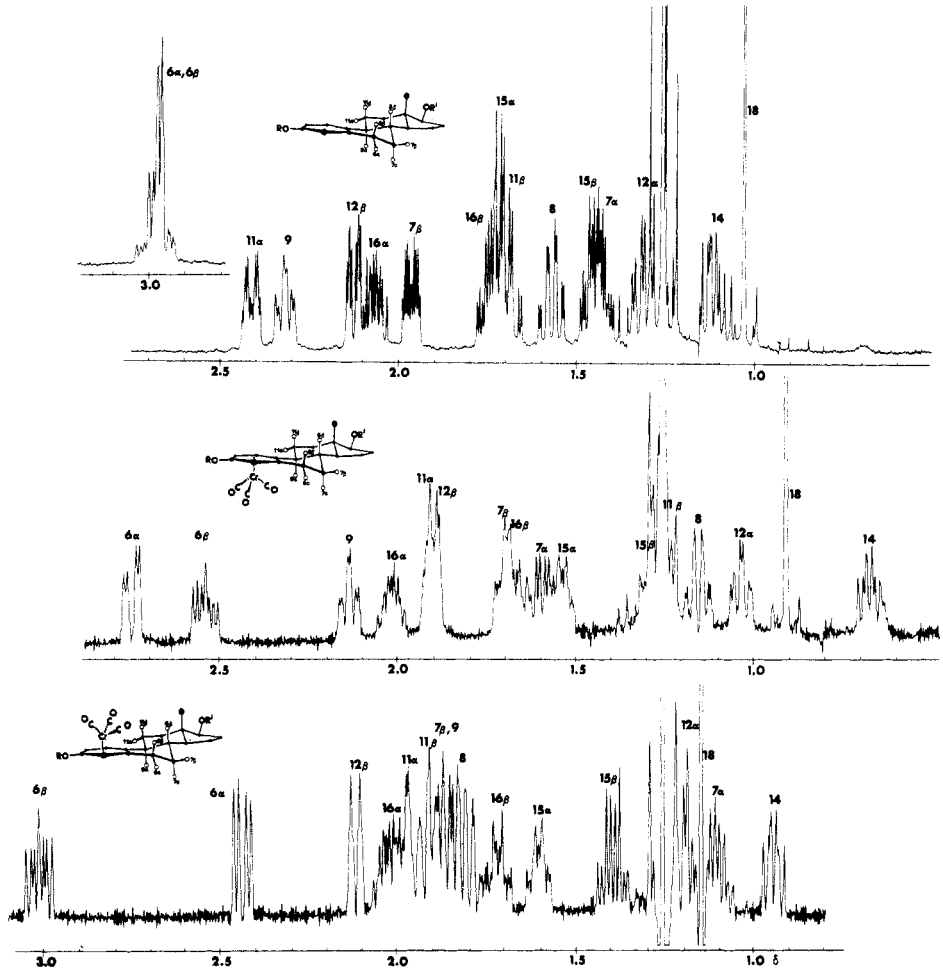


Figure 1. Sections of the 500-MHz ^{1}H NMR spectra of the molecules 8, 6, and 7.

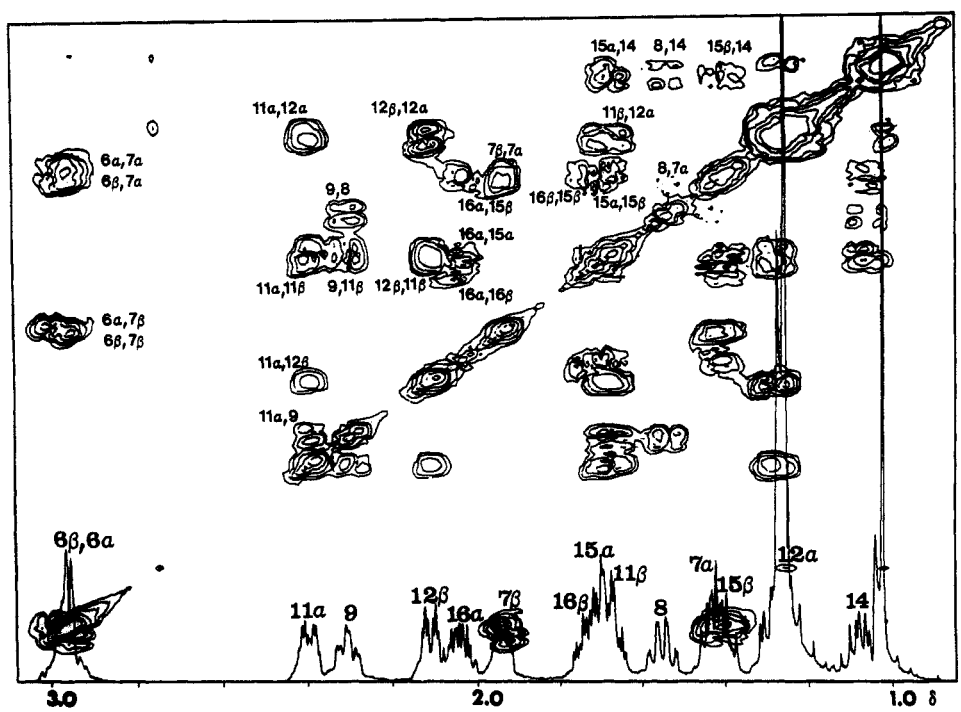


Figure 2. 500-MHz 2-D NMR spectrum of 3-(benzyloxy)-17β-(dimethyl-*tert*-butylsiloxy)-estra-1,3,5(10)-triene, 8. Expanded contour plot of a portion of the matrix for a COSY experiment. The matrix has been symmetrized.

methylene protons H-11α and H-11β. The magnitude of the observed couplings and simulation of the spectrum revealed all the proton shifts and their stereochemical relationship; the former are presented in Table II, and Tables III and IV summarize the coupling constant data.

The detailed analysis of the proton spectrum revealed 22 vicinal coupling constants in a molecule of well-defined stereochemistry, and it would, therefore, seem pertinent

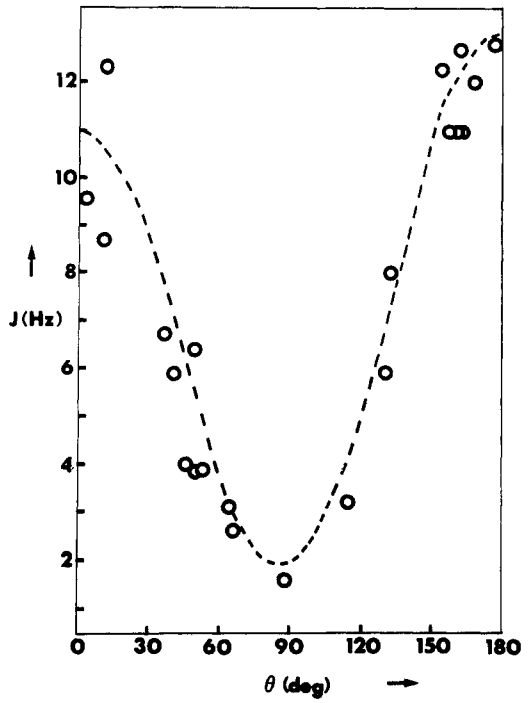


Figure 3. Karplus-type curve relating the vicinal $^3J_{HH}$ coupling constants in 8 with dihedral angles. The dashed line is not fitted to the points but instead is calculated according to eq 1; see text.

to examine the application of a Karplus relationship between $|^3J_{HH}|$, the vicinal coupling constant, and the appropriate dihedral angles. Relationships of this type have been widely invoked despite the cautionary remarks of their progenitor;[11] nonetheless, their use in conformational analysis is of unquestionable value.[12] In Figure 3 is shown a plot of vicinal coupling constants vs. dihedral angles calculated from the crystallographic data for β-estradiol.[5] The dashed line superimposed upon the data is that calculated from the very widely used Karplus relationship proposed by Bothner-By,[13] viz.

$$J = 7 - \cos\theta + 5\cos 2\theta \qquad (1)$$

The experimental data presented in this paper for a steroidal system with five- and six-membered rings incorporating aryl and trialkylsiloxy substituents shows remarkably good correlation with that of the model system, a H–C–C–H fragment in a carbon chain.

In general there is excellent agreement between the proton chemical shift data presented in Table II for the estradiol derivative 8 and the data reported by Hall and Sanders for 1-dehydrotestosterone and 11β-hydroxyprogesterone.[9] However, some controversy exists in the literature concerning the carbon-13 chemical shift assignments of the methylene carbons C-6, C-7, and C-11.[4a,14] The C-6 moiety may easily be identified by the traditional selective $^{13}C\{^1H\}$ experiment through irradiation of the proton resonance at 2.98 ppm. However, the complexity of the proton systems associated with the C-7 and C-11 moieties and the close proximity of other resonances in the ^1H spectrum might indicate that any selective decoupling experiment would be tedious, and ultimately ambiguous.

The two-dimensional $^{13}C\{^1H\}$ heteronuclear chemical shift correlation experiment, however, allows a completely

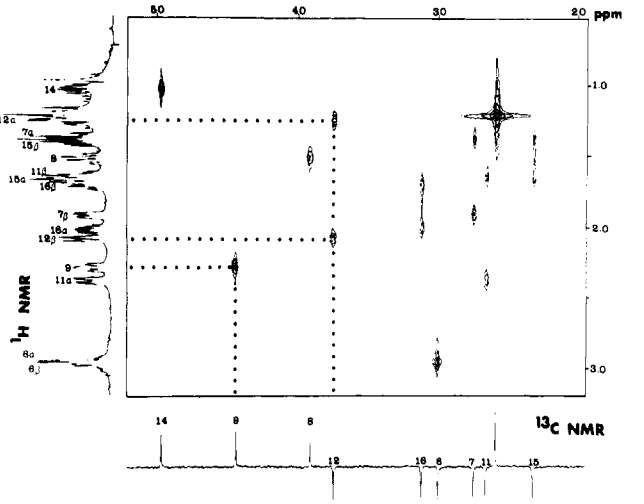


Figure 4. A partial 2-D heteronuclear chemical shift correlated spectrum of 8. A proton spectrum is projected onto the vertical axis; on the horizontal axis is shown a 1-D DEPT spectrum in which CH and CH_3 moieties have positive phase and CH_2 moieties have negative phase. Note that quaternary carbons do not appear in normal polarization transfer experiments. Assignments are discussed in the text.

unambiguous assignment of the carbon spectrum from the proton spectrum. The 2-D matrix which results from the heteronuclear shift-correlated experiment is shown in Figure 4; structural correlations between directly bonded carbon and proton nuclei are revealed. For example, the C-9, H-9 correlation gives rise to a single contour corresponding to the carbon chemical shift at 44.3 ppm and the proton shift at 2.32 ppm; in contrast, methylene protons with their characteristic AB spin coupling pattern exhibit two correlations in the proton domain at the carbon chemical shift of the methylene carbon. The internal consistency between all these two-dimensional NMR experiments instills considerable confidence in the assignments which are collected in Tables II and III.

Examination of molecular models of the α- and β-complexes 6 and 7 reveals that the two possible sites of complexation of the $Cr(CO)_3$ moiety should have profoundly different effects on the ^1H and ^{13}C NMR spectra of the steroid. In particular, a $Cr(CO)_3$ group in the β-position would be expected to modify the chemical shifts of the protons at the 6-, 7-, 8-, 9-, and 11-positions and also those in the methyl group at C-13; the complexation shifts should be essentially reversed for the α-isomer.

The 500-MHz ^1H spectra of the α- and β-complexes 6 and 7 are presented in Figure 1. Again, peak overlap is a problem and has to be overcome via a 2-D NMR experiment. In this case, we selected the technique of spin–echo correlated spectroscopy[10e] (SECSY) to establish the proton connectivity, and Figure 5 shows the result for the β-complex 7. In this presentation, the horizontal contour plot along the center of the spectrum is of the 1-D spectrum, i.e., each proton gives a response along the principal axis at $\Delta\delta = 0$, together with one off-axis response for each resonance with which it shares a scalar coupling.[15] To avoid overly complicating the diagram, only one connectivity sequence which relates H-6β, H-6α, H-7β, and H-7α is shown. Similarly, it is clear that the resonance at δ 3.74 (H-17) is strongly coupled to two other nuclei, and so one can unambiguously locate the two protons at the 16-position. The complete assignments are indicated in Figure 1 and Tables II and V.

(11) (a) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11. (b) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.
(12) Booth, H. *Prog. NMR Spectrosc.* **1969**, *5*, 149.
(13) Bothner-By, A. A. *Adv. Magn. Reson.* **1965**, *1*, 195.
(14) (a) Wittstruck, T. A.; Williams, K. I. H. *J. Org. Chem.* **1973**, *38*, 1542. (b) Engelhardt, G.; Schneider, G. Y.; Weisz-Vincze, I.; Vass, A. *J. Prakt. Chem.* **1974**, *316*, 391.
(15) Wernly, J.; Lauterwein, J. *Helv. Chim. Acta* **1983**, *66*, 1576.

Table V. ^{13}C NMR Data (ppm)

	1	2	3	4	5	6	7	8	9	10	11	12	14	15	16
C1	126.66	95.39	94.21	93.71	92.66	93.76	92.77	126.50	126.18	93.91	92.92	99.48	93.83	92.85	126.24
C2	113.24	79.18	77.95	77.89	76.30	78.13	76.54	112.38	117.27	82.15	80.94	85.80	82.15	80.79	117.27
C3	155.41	141.46	141.80	141.53	141.99	141.70	142.16	157.75	153.46	139.12	139.65	135.51	138.97	139.58	153.46
C4	115.63	80.83	81.21	78.98	79.52	79.27	79.65	115.04	120.06	83.97	84.13	88.19	83.90	83.97	120.06
C5	138.25	113.24	113.24	111.41	111.83	111.58	111.97	138.57	137.94	111.74	112.12	115.92	111.66	112.04	138.05
C6	30.11	30.38	28.14	30.01	27.73	30.19	27.92	30.22	29.63	29.63	27.61	29.43	30.04	27.68	29.74
C7	27.96	26.34	27.45	25.65	26.43	25.94	26.63	27.67	27.34	25.79	26.39	25.68	25.94	26.55	27.44
C8	39.73	39.66	38.66	38.77	37.75	38.99	38.00	39.21	38.87	38.91	37.85	38.11	38.99	37.85	38.98
C9	44.70	43.84	43.40	43.01	42.55	43.24	42.86	44.30	44.06	43.08	42.55	42.13	43.24	42.78	44.28
C10	132.12	105.09	107.52	105.01	107.39	105.52	107.89	133.57	133.24	105.06	107.41	109.05	105.21	107.49	133.45
C11	26.98	26.98	26.45	26.20	25.83	26.70	25.94	26.75	26.30	26.55	25.79	26.14	26.62	25.87	26.46
C12	37.71	37.01	37.07	36.17	36.15	36.79	36.79	37.53	36.85	36.33	36.26	35.88	36.79	36.71	37.34
C13	43.78	43.69	43.70	43.01	43.12	43.54	43.62	43.89	43.30	43.08	43.16	42.95	43.54	43.54	43.74
C14	50.77	49.56	50.38	49.10	49.63	48.99	49.53	49.68	50.19	49.31	49.76	48.92	48.93	49.46	49.91
C15	23.55	23.41	23.45	22.89	23.01	23.14	23.29	23.47	23.18	22.98	22.98	22.83	23.14	23.21	23.39
C16	30.91	30.77	30.88	30.35	30.49	30.95	30.95	31.13	30.62	30.49	30.42	30.25	30.95	30.87	31.11
C17	81.66	81.29	81.60	81.37	81.61	81.56	81.70	81.82	81.95	81.55	81.55	81.33	81.55	81.62	81.95
C18	11.29	11.23	11.20	11.06	10.97	11.38	11.30	11.57	11.10	11.07	10.92	10.96	11.38	11.15	11.43
$(CH_3)_2$	*a*					-4.40	-4.40	-4.34	-4.37	-4.40	-4.47	-4.45	-4.47	-4.47	-4.32
						-4.78	-4.70	-4.68	-4.37	-4.40	-4.47	-4.45	-4.77	-4.85	-4.76
C-O		235.18	235.78	*b*	*b*	234.25	234.78			234.40	234.93	*b*	234.40	234.85	

[a] These methyl groups are diastereotopic. [b] Not observed.

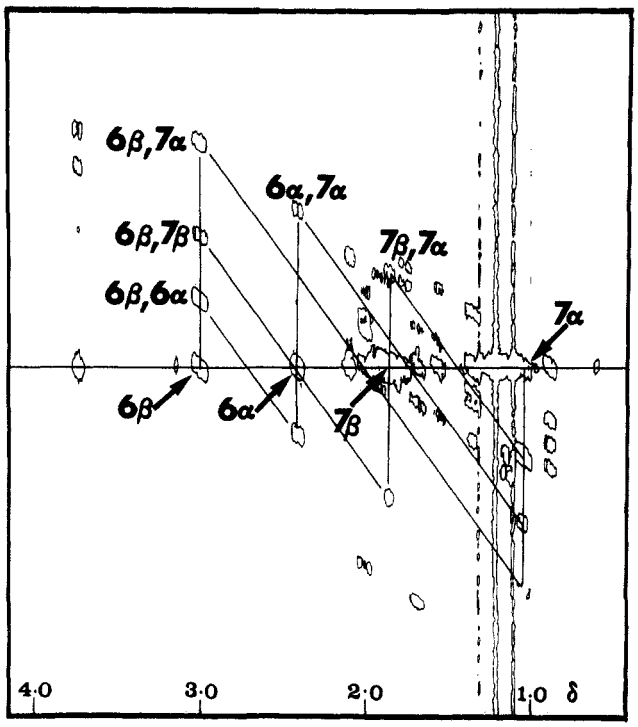


Figure 5. 500-MHz ^1H shift correlated 2-D spectrum of the β-complexed steroid 7; contour plot representation of the SECSY experiment. The 500-MHz 1-D spectrum of 7 appears as the lowest trace of Figure 1.

The effects of complexation by $Cr(CO)_3$ on the proton shifts of the steroid 8 exceeded our expectations and fully justified the effort expended in assigning all the peaks. The protons in the aromatic ring exhibited the approximately 2-ppm shielding effect so typical of such systems.[16] The most obvious and esthetically satisfying result is the clear differentiation of the 6α- and 6β- protons. In the free arene 8, these two nuclei have almost identical chemical shifts while in the α-complex the 6β-proton is shielded by 0.2 ppm relative to its partner; the β-complex shows a spectacular reversal and the chemical shift difference between these geminal protons is now more than 0.5 ppm!

It is clear that the shielding of the protons distal to the $Cr(CO)_3$ group and concomitant deshielding of the proximal protons is a consequence of the magnetic anisotropy of the tripodal moiety. Such effects have been noted previously: in $Cr(CO)_3$ complexes of 1-methylindanes or of 2-methylindanones, the methyl protons exo to the organometallic fragment are shielded relative to their endo partners.[6,17] Other striking examples are provided by the hexaethylbenzene complexes of $M(CO)_3$, where M = Cr, Mo, or W. In these systems, the ethyl groups project alternately above and below the plane of the arene so as to avoid the tripodal carbonyl groups and it is the proximal methylene groups which resonate at highest frequency.[18] In the simplest model, we can regard the magnetic anisotropy of the $Cr(CO)_3$ group as arising from the summation of the anisotropies of the individual carbonyl ligands. Thus, protons along or close to the C_∞ axis of a CO group will experience a profound shielding effect as is well-known for the alkyne linkage.[19] Conversely, nuclei situated near the plane perpendicular to the carbon–oxygen bond will be markedly deshielded. These ideas are remarkably well borne out by the data in Figure 1 and Table II. Thus, for the β-complex 7, the proximal protons at H-8 and H-11β are deshielded by ~0.25 ppm while the protons of the methyl group at C-13 are deshielded by 0.12 ppm; in contrast, the distal hydrogen nuclei at 6α, 7α, 9, 11α, 12α, and 14 should be, and indeed are, substantially shielded. However, for the α-isomer we observe shielding for the 6β-, 7β-, 8-, 11β-, 12β-, and 18-methyl protons and deshielding for the 7α-proton. Interestingly, the H-14 and H-11α resonances in the α-isomer are significantly shielded (by 0.42 and 0.48 ppm, respectively) despite the fact that they are on the same face of the molecule as the metal carbonyl fragment. Closer examination of the structure reveals, however, that the pronounced arching of the steroidal skeleton pushes these latter two protons into the shielding zone of the tripodal group. A complete mathe-

(16) (a) Farnell, L. F.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc. D* **1971**, 1078. (b) Mann, B. E. *J. Chem. Soc. D* **1971**, 976. (c) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012.

(17) Jaouen, G.; Meyer, A. *J. Am. Chem. Soc.* **1975**, *97*, 4667.

(18) (a) McGlinchey, M. J.; Bougeard, P.; Sayer, B. G.; Hofer, R.; Lock, C. J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 634. (b) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

(19) (a) Reddy, G. S.; Goldstein, J. H. *J. Chem. Phys.* **1963**, *39*, 3509. (b) Agarwal, A.; McGlinchey, M. J. *Can. J. Chem.* **1978**, *56*, 959. (c) McGlichey, M. J.; Burns, R. C.; Hofer, R.; Top, S.; Jaouen, G. *Organometallics*, accepted for publication.

matical treatment of this phenomenon together with an evaluation of χ, the diamagnetic anisotropy of the $Cr(CO)_3$ group, is deferred to another paper.[19c]

The ^{13}C NMR data for the molecules **1** through **16** are collected in Table V and show that complexation by a tricarbonylchromium(0) group has little effect on the carbon nuclei distant from the site of attachment of the organometallic moiety. As is well-known for π-complexes of arenes,[20] there is a sizeable shielding of the aromatic carbons relative to their resonance positions in the free ligand; the reasons for this have been discussed extensively elsewhere.[21] In the molecules described herein, both the α- and β-complexes show similar effects for most resonances. There are some small differences, however. At positions C-2, C-6, and C-10, the peaks for the α- and β-isomers show a difference of ca. 2 ppm. At the 2- and 6-positions, it is the β-isomer which has the more shielded absorptions while, for the C-10 resonance, the reverse is true. At present, we prefer not to speculate as to why this should be the case and merely report the observation. However, it is clear that ^{13}C chemical shifts cannot be gainfully employed to identify unambiguously a given diastereomer.

To conclude, an examination of the high-resolution ^1H NMR spectrum of the $Cr(CO)_3$ complexes of estradiol and its derivatives allows ready differentiation of the α- and β-isomers. We are continuing our synthetic and structural studies on organometallic derivatives of steroidal hormones, and they will be the subject of further reports.

Experimental Section

NMR spectra were acquired at 11.74 T using Bruker AM500 and WM500 spectrometers. The 500-MHz proton spectra and 125.7-MHz carbon spectra were observed by using proton and proton/carbon dual probeheads, respectively. All spectra were recorded at 300 K and all chemical shifts measured relative to the chemical shift of tetramethylsilane. Homonuclear chemical shift correlation (COSY) experiments were carried out by using the pulse sequence: delay – $(\pi/2,^1H)$ – t_1 – $(\pi/2,^1H)$ – acquisition. Pulses were phase cycled according to ref 22. A 2-s recycle delay was used: the $\pi/2,^1H$ pulse was 8 μs. A total of 32 transients was collected per unit time; 256 time increments of 1 ms were applied to characterize the t_1 domain, and 1024 points were used to characterize t_2. A pseudoecho window function was applied in both t_1 and t_2 following zero filling once in the t_2 domain.

Heteronuclear chemical shift correlated spectra were obtained by using the pulse sequence: delay – $(\pi/2,^1H)$ – $(t_1/2)$ – $(\pi,^{13}C)$ – $(t_1/2)$ – Δ_1 – $(\pi/2, ^1H; \pi/2, ^{13}C)$ – Δ_2 – acquisition with decoupling. All pulses were phase cycled according to ref 22. A 2-s recycle delay was used, and the delay times $\Delta_1 = {}^1/_{2}J$ and $\Delta_2 = {}^1/_{4}J$ were calculated from a compromise value of $^1J(C,H) = 125$ Hz. The $\pi/2,^1H$ pulse was 20 μs and the $\pi/2,^{13}C$ pulse was 10 μs. The spectral width in the t_2(carbon) domain was 15 151 Hz and in the t_1(proton) domain was 4000 Hz; 1024 points were used in both t_1 and t_2 and Gaussian enhancement of the data was applied.

SECSY and edited DEPT spectra were obtained as described in ref 10e and 23. Spectral simulation was undertaken by using the commercially available Bruker PANIC program. Optical rotations were recorded on a Perkin-Elmer 241MC or 241 model. All syntheses of organometallic complexes were carried under a dry nitrogen atmosphere. Tetrahydrofuran and benzene were freshly distilled from sodium–benzophenone immediately before use.

α- and β-(Estradiol)tricarbonylchromium, 2 and 3. β-Estradiol (1.36 g, 5.0 mmol) and $Cr(CO)_6$ (2.2 g, 10.0 mmol) were heated under reflux in dibutyl ether (150 mL) during 6 h. After filtration and evaporation of solvent, the resulting yellow oil was rapidly chromatographed on silica gel plates using ether/petroleum ether (4:1) as eluent. The first fraction was extracted in ether, immediately recrystallized from ether/heptane, and yielded yellow crystals of **2** (250 mg, 0.61 mmol; 12.2%), $|\alpha|^{21}_D$ +45° (acetone, *c* 0.02 g/mL). The product was characterized by ^{13}C NMR spectroscopy; the product decomposed on the Kofler block. In like manner, the second fraction gave **3** (300 mg, 0.74 mmol; 14.7%), $|\alpha|^{21}_D$ +54.3° (acetone, *c* 0.026 g/mL).

α- and β-(3-(Benzyloxy)-17β-hydroxyestra-1,3,5(10)-triene)tricarbonylchromium, 4 and 5. β-Estradiol (2.72 g, 10.0 mmol) and $Cr(CO)_6$ (4.4 g, 20.0 mmol) were heated under reflux in dibutyl ether (170 mL) during 8 h. After filtration and evaporation of solvent, the resulting yellow residue was dissolved in THF (20 mL). Following the method of Czernecki et al.,[24] this solution was carefully added to a suspension of 50% NaH (0.75 g, 15.5 mmol) and stirred for 5 h after which time benzyl bromide (8.5 g, 50 mmol) was introduced and the mixture heated under reflux during 5 h. The reaction mixture was left at ambient temperature overnight, then hydrolyzed with ice water, extracted with ether, and again washed with water and the ethereal solution dried over magnesium sulfate. The product was then chromatographed on a silica gel (Merck 7731) column and eluted with ether/petroleum ether (2:1). The first fraction was identified as **4** (1.22 g, 2.45 mmol; 24.5%): mp 185 °C; $|\alpha|^{21}_D$ +28.5° ($CHCl_3$, *c* 0.0026 g/mL). Calcd for $C_{28}H_{30}O_5Cr$: C, 67.45; H, 6.06. Found: C, 66.10; H, 6.00. The second fraction was identified as **5** (996 mg, 2.0 mmol; 20.0%): mp 186 °C; $|\alpha|^{21}_D$ +84° ($CHCl_3$, *c* 0.002 g/mL). Calcd for $C_{28}H_{30}O_5Cr$; C, 67.45; H, 6.06. Found: C, 67.51; H, 6.15.

α- and β-(3-(Benzyloxy)-17β-(dimethyl-*tert*-butylsiloxy)estra-1,3,5(10)-triene)tricarbonylchromium, 6 and 7. A solution of **4** (1.5 g, 3.0 mmol) in THF (20 mL) was carefully added to a suspension of 50% NaH (1.3 g, 27.1 mmol) in THF (20 mL). The mixture was stirred overnight at ambient temperature and then heated under reflux during 2 h. *t*-$BuMe_2SiCl$[25] (1.5 g, 10.0 mmol) was added to the solution, and the temperature was maintained for another 2.5 h. After hydrolysis with ice water, ether extraction, and solvent removal, the residue was chromatographed on a silica gel (Merck 9385) column using ether/petroleum ether (1:10) as eluent. The yellow solid was identified as **6** (1.23 g, 2.01 mmol; 67%): mp 174 °C; $|\alpha|^{21}_D$ +35° ($CHCl_3$, *c* 0.003 g/mL). The mass spectrum showed peaks at *m/z* 612 $[M]^+$, 528 $[M - 3CO]^+$, and 476 $[M - Cr(CO)_3]^+$.

Analogously, **5** (1.2 g, 2.4 mmol), 50% NaH (1.0 g, 20.8 mmol) and *t*-$BuMe_2SiCl$ (1.05 g, 7.0 mmol) yielded **7** (800 mg, 1.31 mmol; 55.0%): mp 180 °C; $|\alpha|^{21}_D$ +53.3° ($CHCl_3$, *c* 0.003 g/mL). The mass spectrum showed peaks at *m/z* 612 $[M]^+$, 528 $[M - 3CO]^+$, and 476 $[M - Cr(CO)_3]^+$.

3-(Benzyloxy)-17β-(dimethyl-*tert*-butylsiloxy)estra-1,3,5(10)-triene, 8. The diprotected complex **6** (306 mg, 0.5 mmol) was dissolved in ether and exposed to sunlight during 2 h.[26] After filtration and evaporation of the solvent, the residual white solid was recrystallized from ether/petroleum ether and identified as **8** (214 mg, 0.45 mmol; 90%): mp 139 °C; $|\alpha|^{21}_D$ +39.6° ($CHCl_3$, *c* 0.010 g/mL). The mass spectrum showed peaks at *m/z* 476 $[M]^+$ and 419 $[M - t\text{-}Bu]^+$.

3-(Dimethyl-*tert*-butylsiloxy)-17β-hydroxyestra-1,3,5(10)-triene, 9. A solution of β-estradiol (5.54 g, 20.0 mmol) in THF (40 mL) was carefully added to a suspension of 50% NaH (1.2 g, 25.0 mmol) in THF (40 mL). The mixture was stirred during 0.5 h, then *t*-$BuMe_2SiCl$[25] (3.5 g, 23.3 mmol) was added to the solution, and the stirring was maintained for another 3 h. After hydrolysis with ice water, extraction with CH_2Cl_2, and solvent removal, the residue was recrystallized from petroleum ether. The white solid was identified as **9** (5.7 g, 14.7 mmol; 73%),

(20) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.
(21) Maricq, M. M.; Waugh, J. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 6902 and references therein.
(22) Bax, A.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 501.
(23) (a) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323. (b) Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.
(24) Czernecki, S.; Georgoulis, C.; Provelenghiou, C. *Tetrahedron Lett.* **1976**, 3535.
(25) (a) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190. (b) Arzano, H. B.; Barton, D. H. R.; Davies, S. G.; Lusinchi, X.; Meunier, B.; Pascard, C. *Nouv. J. Chim.* **1980**, *4*, 369.
(26) Jaouen, G.; Dabard, R. *Tetrahedron Lett.* **1971**, 1015.

mp 158 °C. Anal. Calcd for $C_{24}H_{38}O_2Si$: C, 74.57; H, 9.91. Found: C, 74.95; H, 9.97.

α- and β-(3-(Dimethyl-*tert*-butylsiloxy)-17β-hydroxyestra-1,3,5(10)triene)tricarbonylchromium, 10 and 11. Monosilylated estradiol **9** (3.2 g, 8.3 mmol) and $Cr(CO)_6$ (3.7 g, 16 mmol) were heated under reflux in dibutyl ether (150 mL) during 8 h. After filtration and solvent removal, the residue was chromatographed on a silica gel (Merck 7734) column using ether/petroleum ether (1:1) as eluent. The first fraction was identified as **10** (1.27 g, 2.4 mmol; 29%), mp 220 °C. Anal. Calcd for $C_{27}H_{38}O_5CrSi$: C, 62.05; H, 7.33. Found: C, 61.82; H, 7.27. The second fraction was identified as **11** (1.8 g, 3.4 mmol; 41.5%), mp 179 °C. Anal. Calcd for $C_{27}H_{38}O_5CrSi$: C, 62.05; H, 7.33. Found: C, 62.00; H, 7.30.

α- and β-(3-(*tert*-Butyldimethylsiloxy)-17-hydroxyestra-1,3,5(10)-triene)dicarbonyl(thiocarbonyl)chromium, 12 and 13. Following the method of Jaouen et al.,[27] the $Cr(CO)_3$ complex **10** (0.52 g, 1.0 mmol) was photolysed in benzene/cyclooctene (150 mL/25 mL) and treated with triphenylphosphine (1 g) and CS_2 (25 mL). After removal of solvent, the residue was chromatographed on a silica gel (Merck 9385) column using ether/petroleum ether (3:2) as eluent. The yellow solid was identified as **12** (0.06 g, 0.11 mmol; 11%), mp 142 °C. The mass spectrum showed peaks at m/z 482 $[M - 2CO]^+$ and 386 $[M - Cr(CO)_2CS]^+$. The molecule **12** was identified by X-ray crystallography.[7] Likewise, **11** yielded **13** (35%), mp 125 °C. The mass spectrum showed peaks at m/z 482 $[M - 2CO]^+$, 438 $[M - 2CO - CS]^+$, and 386 $[M - Cr(CO)_2CS]^+$.

(27) Jaouen, G.; Simonneaux, G. *Inorg. Synth.* **1979**, *XIX*, 197.

α- and β-(3,17β-Bis(dimethyl-*tert*-butylsiloxy)estra-1,3,5(10)-triene)tricarbonylchromium, 14 and 15. As with the corresponding benzyl analogues, the monosilylated estradiol complex **10** (7.5 g, 14 mmol) was treated with 50% NaH (6.72 g, 140 mmol) and *t*-$BuMe_2Cl$ (6.39 g, 43 mmol). The yellow solid obtained after chromatography (silica gel column (Merck 7734), using ether/petroleum ether (1:10) as eluent) was identified as **14** (8.7 g, 13.6 mmol; 96%), mp 255 °C. Calcd for $C_{33}H_{52}O_5CrSi_2$: C, 62.22; H, 8.23. Found: C, 62.32; H, 8.27. The mass spectrum showed peaks at m/z 636 $[M]^+$, 580 $[M - 2CO]^+$, 552 $[M - 3CO]^+$, and 500 $[M - Cr(CO)_3]^+$. Analogously, **15** was obtained from **11** (93%), mp 253 °C. Anal. Calcd for $C_{33}H_{52}O_5CrSi_2$: C, 62.22; H, 8.23. Found: C, 61.98; H, 8.40. The mass spectrum showed peaks at m/z 636 $[M]^+$, 580 $[M - 2CO]^+$, 552 $[M - 3CO]^+$, and 500 $[M - Cr(CO)_3]^+$.

3,17β-Bis(dimethyl-*tert*-butylsiloxy)estra-1,3,5(10)-triene, 16. The disilylated complex **14** (or **15**) (636 mg, 1.0 mmol) was dissolved in ether and exposed to sunlight during 3 h.[26] After filtration and evaporation of the solvent, the residual white solid was recrystallized from ether/petroleum ether and identified as **16** (425 mg, 0.85 mmol; 85%), mp 120 °C.

Acknowledgment. We thank the C.N.R.S. (France) and N.S.E.R.C. (Canada) for financial support.

Registry No. **1**, 50-28-2; **2**, 77109-92-3; **3**, 98757-31-4; **4**, 98688-30-3; **5**, 98757-32-5; **6**, 88729-93-5; **7**, 88765-18-8; **8**, 98688-31-4; **9**, 57441-02-8; **10**, 93036-14-7; **11**, 98757-33-6; **12**, 93173-93-4; **13**, 98757-34-7; **14**, 91795-23-2; **15**, 91841-08-6; **16**, 57711-41-8; $Cr(CO)_6$, 13007-92-6.

Intermolecular Formation of C–H Bonds: Application to the Synthesis of Heterobimetallic Complexes

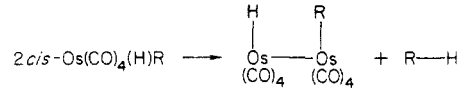
Keith E. Warner and Jack R. Norton*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received May 21, 1985

The reactions of various alkylmetal carbonyl complexes (e.g., $MeMn(CO)_5$, $EtRe(CO)_5$, $MeFe(CO)_2Cp$, $Me_2Os(CO)_4$) with various transition-metal hydrides (e.g., $HRe(CO)_5$, $H_2Os(CO)_4$, $HMn(CO)_5$, $HW(CO)_3Cp$) have been examined in solvents of different coordinating abilities. In coordinating solvents the metal-containing products are solvated dinuclear complexes; in noncoordinating solvents the metal-containing products are polynuclear hydrides, formed by the coordination of a second equivalent of the hydride reactant. The vacant coordination site is created on the metal that originally bears the alkyl ligand: in CH_3CN, $MeMn(CO)_5$ and $HRe(CO)_5$ give $(CH_3CN)Mn(CO)_4Re(CO)_5$, whereas $EtRe(CO)_5$ and $HMn(CO)_5$ give $(CH_3CN)Re(CO)_4Mn(CO)_5$. The organic products eliminated are generally aldehydes (although alkane elimination is also seen, particularly when the initial alkyl carbonyl complex is a dialkyl). The reaction is fastest in coordinating solvents and for the alkyl carbonyl complexes that most readily form acyls: $MeMn(CO)_5$ and those complexes of other metals (e.g., $EtRe(CO)_5$) that contain alkyl groups that migrate more readily than methyl. When heated in acetonitrile solution, $EtRe(CO)_5$, *i*-$BuRe(CO)_5$, and some other alkyl carbonyl complexes equilibrate with solvated acyl complexes such as *cis*-$RC(O)(CH_3CN)Re(CO)_4$; these solvated acyl complexes react rapidly at low temperatures with hydrides to eliminate aldehydes. In favorable cases, the reactions of alkyl carbonyls with transition-metal hydrides are synthetically attractive routes to heterobimetallic complexes.

The intermolecular formation of C–H bonds from alkyl carbonyl complexes and transition-metal hydrides has attracted the attention of several research groups. We have shown that alkane elimination from *cis*-$Os(CO)_4(H)R$ according to eq 1 is intermolecular, and have proposed that



(1)

the rate-determining step is the formation of a coordinatively unsaturated acyl intermediate from *cis*-$Os(CO)_4(H)R$.[1] Bergman and co-workers[2] have proposed that rate-determining formation of an acyl from $CpMo(CO)_3R$ precedes the formation of aldehydes in eq 2. Halpern and co-workers[3] have proposed that rate-determining formation

$$CpMo(CO)_3R + CpMo(CO)_3H \rightarrow RCHO + {}^1/_2Cp_2Mo_2(CO)_6 + {}^1/_2Cp_2Mo_2(CO)_4 \quad (2)$$

R = Me, Et

(1) (a) Okrasinski, S. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 295. (b) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (c) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376.

(2) (a) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

0276-7333/85/2304-2150$01.50/0