a photomultiplier-based photon-counting detector. A red-sensitive Hamamatsu R928 photomultiplier tube was used for these measurements.

The obtained emission and excitation spectra were fully corrected for variations in the detector response and exciting lamp intensity as a function of wavelength; the band maxima were reproducible to ±4 nm. Excitation data were recorded from solutions that were optically dilute ($A < 0.1$) throughout the spectral region; under these conditions excellent agreements were observed between the absorption and excitation data for known standards such as quinine sulfate and 1,2-benzanthracene.[16] Emission quantum yields (ϕ_e) were determined by the Parker-Rees method[17] with dilute $Ru(bpy)_3^{2+}$ in deoxygenated aqueous solution at 283 K ($\phi_e = 0.046$)[18] as a calibrant. These values were corrected for the differing refractive indices of the solvents,[19] and they are believed to be accurate to ±10%. In all the emission and excitation experiments the sample solutions were filtered through 0.22-μm Millipore filters and deoxygenated prior to taking readings. The solution temperature was controlled to ±0.1 K. Solvent blanks were also run to check for possible emitting impurities.

Emission lifetimes (τ_e) were determined on a PRA System 3000 time-correlated pulsed single-photon apparatus that is described more fully in an earlier paper.[3] Solutions were excited in the 300–400 nm region with monochromatic light from a PRA Model 510 nitrogen flash lamp, typically using a lamp pulse width of 1 ns. Single exponential decays were observed for each sample, and the lifetime errors were estimated to be ±5 ns. The reported values represent the average of at least three readings.

Electrochemical Studies. Cyclic voltammetry data were recorded on a BioAnalytical Systems Corrosion Model CV-47 voltammograph connected to a Houston Instruments Model 200 X-Y recorder. The electrochemical cell contained a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). The concentrations of the metal carbonyl complexes in these experiments were in the 10^{-3}–10^{-4} M range, and 0.1 M tetrabutylammonium perchlorate (TBAP) was present as the supporting electrolyte. The measurements were uncorrected for the liquid-junction potentials, but these are estimated to be less than 0.01 V. The ferrocene–ferrocenium ($F_c/F_c^+ = 0.466$ V) oxidation was used as an internal standard,[13c,20] and the reported potentials are calibrated to this value. The scan rate used in these experiments was 80 mV s^{-1}. In all cases absorption spectra recorded following electrochemical measurements were unchanged, indicating negligible complex decomposition.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. MMZ gratefully acknowledges receipt of a South African CSIR fellowship and support from the United Nations. We also thank Prof. B. McDuffie for the use of the electrochemical apparatus.

Registry No. $ClRe(CO)_4(pyz)$, 119325-59-6; $ClRe(CO)_4(pyz)^-$, 119325-64-3; $ClRe(CO)_4(pyz)^{2-}$, 119325-67-6; $(OC)_5W(pyz)W(CO)_5$, 70738-71-5; $(OC)_5W(pyz)W(CO)_5^-$, 79070-32-9; $(OC)_5W(pyz)W(CO)_5^{2-}$, 119325-65-4; $Cl(OC)_4Re(pyz)Re(CO)_4Cl$, 119325-60-9; $Cl(OC)_4Re(pyz)Re(CO)_4Cl^-$, 119325-68-7; $Cl(OC)_4Re(pyz)Re(CO)_4Cl^{2-}$, 119325-69-8; $Cl(OC)_4Re(pyz)Re(CO)_4Cl^{3-}$, 119325-70-1; $(OC)_5W(pyz)Re(CO)_4Cl$, 119325-61-0; $(OC)_5W(pyz)Re(CO)_4Cl^-$, 119325-62-1; $(OC)_5W(pyz)Re(CO)_4Cl^{2-}$, 119325-66-5; $W(CO)_5(pyz)$, 65761-19-5; $W(CO)_5(pyz)^-$, 119325-63-2; $ClRe(CO)_5$, 14099-01-5; $W(CO)_5(THF)$, 36477-75-5; pyz, 290-37-9; pyz^-, 34512-20-4.

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(Cyclopentadienyl)ruthenium Complexes of 3-Methoxyestrone: A High-Field NMR and X-ray Crystallographic Study

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The α- and β-stereoisomers of (η^6-estrone 3-methyl ether)(η^5-cyclopentadienyl)ruthenium(II) hexafluorophosphate have been synthesized by thermal ligand exchange between (cyclopentadienyl)tris(acetonitrile)ruthenium hexafluorophosphate and estrone 3-methyl ether. The initial 7:3 α:β mixture was fractionally crystallized to yield each pure stereoisomer. ^1H and ^{13}C NMR spectra were analyzed in detail for each stereoisomer, and an X-ray structure for the β-isomer of $(C_{19}H_{24}O_2)Ru(C_5H_5)^+PF_6^-$ was carried out: monoclinic; $P2_1$; $a = 8.0717$ (7) Å, $b = 14.813$ (1) Å, $c = 10.597$ (1) Å; $\beta = 109.93$ (1)°; $Z = 2$. The structure was refined to R and R_w values of 0.0251 and 0.0325, respectively, by using 1989 reflections.

Introduction

In recent years, there has been burgeoning interest in the use of organometallic moieties to modify the chemistry of steroidal systems.[1] Typically, the $Fe(CO)_3$ fragment has been used to protect the diene unit in the B ring of ergosterol and related plant steroids; this permitted the facile manipulation of the C(22)–C(23) double bond.[2] Likewise, (η^3-allyl)palladium and η^6-$Cr(CO)_3$ groups have

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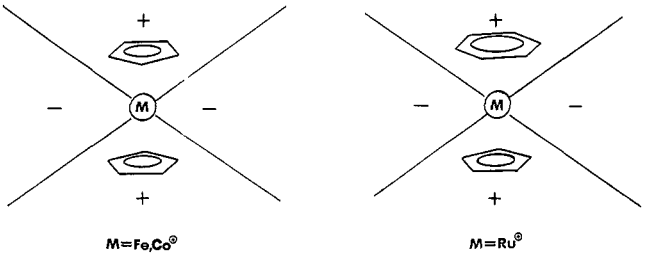


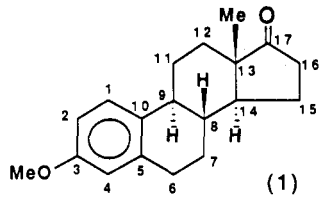
Figure 1. Shielding and deshielding zones for Cp_2M, where M = Fe or Co^+, and for ArMCp, where M = Ru^+.

also been exploited for synthetic purposes.[3,4] A particularly fascinating concept, which has been pioneered by Jaouen and his co-workers,[5] involves the incorporation of metal carbonyl units into steroidal hormones. Thus, the diastereomeric complexes of estradiol in which a $Cr(CO)_3$ fragment is π-bonded to either the α- or the β-face of the aromatic A ring have been thoroughly characterized.[6] Furthermore, when an alkynyl substituent is attached at the 17α-position, as in 17α-ethynyl-3-methoxyestradiol (Mestranol)—a commercially available steroidal contraceptive, facile incorporation of a hexacarbonyldicobalt unit has been accomplished.[7] In these complexes, the very intense metal carbonyl ν_{CO} infrared vibrations have been used to assay hormonal receptor sites; this novel technique promises to be an invaluable tool for the early detection of breast cancer.[8]

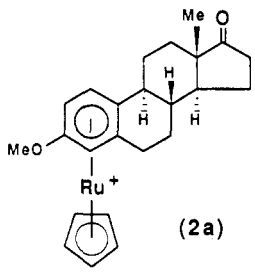
It has recently been shown that when a cationic $(C_5H_5)Ru$ moiety is attached to an aromatic ring which bears a halogen or other potential leaving group the propensity of the aromatic ring to undergo nucleophilic substitution with concomitant loss of halide is greatly enhanced.[9] This technique has been turned to synthetic advantage in the preparation of a series of functionalized indoles, including some of biological importance.[10] The $CpRu^+$ moiety can also be incorporated into estrogenic steroidal systems since these possess an aromatic ring to which the organometallic moiety can coordinate.

These molecules are of interest to the NMR spectroscopist not merely because they pose challenges of spectral assignment but also because they contain organometallic moieties suitably positioned so as to probe the effect of the metal fragment on the chemical shifts of neighboring protons. In principle, this may allow evaluation of the diamagnetic anisotropy of the organometallic unit; in turn, such parameters can be used to aid in the structural characterization of other molecules containing organometallic substituents.

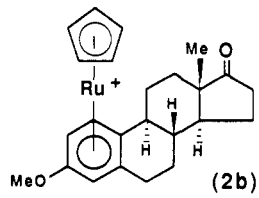
We here describe the synthesis and separation of the α-$(C_5H_5)Ru^+$ and β-$(C_5H_5)Ru^+$ complexes of estrone 3-methyl ether **1** together with a complete ^1H and ^{13}C NMR investigation of both complexes **2a** and **2b**. Moreover, the β-diastereomer has been unequivocally identified via an X-ray crystallographic study.



(1)



(2a)



(2b)

Results and Discussion

It has been elegantly demonstrated by Jaouen that the placement of a $Cr(CO)_3$ group on a particular face of the aromatic ring of a steroid skeleton not only enhances the acidity of the benzylic position but also controls which proton is removed. By this means, it is possible specifically to incorporate a functional group by replacing one hydrogen of a methylene pair.[4] However, using the conventional chiroptical methods, it is by no means trivial to determine to which face of the steroid an organometallic fragment is bonded. Since it is impractical to obtain X-ray crystallographic data for each system, NMR methods have been developed which allow one to distinguish between the α- and β-diastereomers.[6] One such method utilizes the diamagnetic anisotropy of the metal carbonyl ligands. Terminal M—C≡O linkages are, of course, linear and resemble alkynes[11] in that protons sited along or close to the triple-bond axis experience a marked shielding effect; in contrast, those nuclei which lie close to the plane orthogonal to this axis are noticeably deshielded.[12] The simplest mathematical model uses the McConnell equation[13] which relates the incremental change in chemical shift to χ, the diamagnetic anisotropy of the molecular fragment, via the geometric term

$$\sigma = \chi(1 - 3\cos^2\theta)/3R^3$$

where σ is the incremental shift, χ is the diamagnetic anisotropy of the carbonyl ligand,[12] R is the distance of the proton in question from the center of the C–O bond, and θ is the angle made by this line with the C–O axis. An important point arising from the geometric term is that for values of θ exceeding 54.74° the protons are deshielded while those nuclei positioned such that $\theta < 54.74°$ will be correspondingly shielded. [The generation of cones of anisotropy is a familiar picture for those who have used the ring current model[14] to account for the shifts of protons

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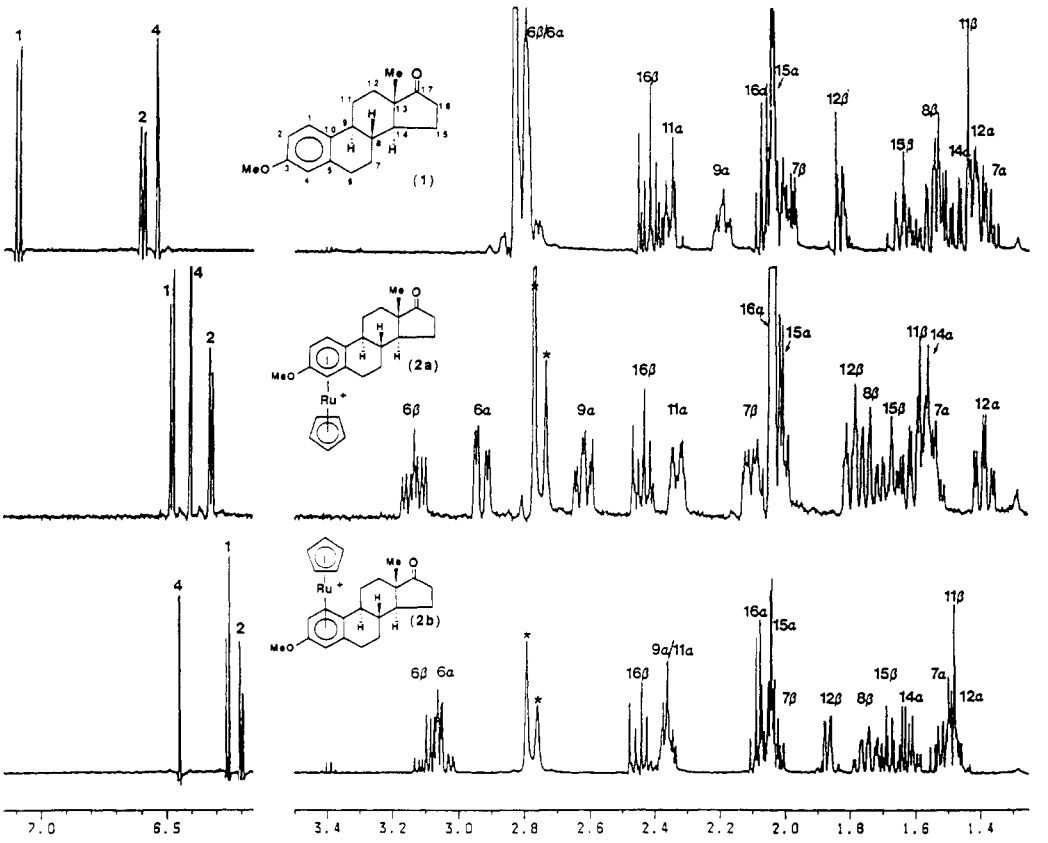

Figure 2. 500-MHz ^{1}H NMR spectra of estrone 3-methyl ether and of its α- and β-$(C_5H_5)Ru^+$ complexes.

in the vicinity of aromatic rings.] Using this approach, it has proven possible to distinguish between the α- and β-isomers of (estradiol)$Cr(CO)_3$.[6] Very recently, the α- and β-$Cr(CO)_3$ complexes of the diterpenoid methyl *O*-methylpodocarpate have also been prepared and separated; once again, the NMR spectroscopic and X-ray crystallographic structural methods are in complete accord.[15]

To return to the molecules in the present study, one could well imagine that sandwich compounds of the general type $(\eta^m\text{-}C_mH_m)M(\eta^n\text{-}C_nH_n)$ would also exhibit similar anisotropic behavior. This gains support from the experimental data on the directly measured anisotropy in diamagnetic susceptibility for ferrocene[16] and also for the cobalticinium system $[(C_5H_5)_2Co]^+$.[17] These studies suggest that the shielding zone lies close to the C_5 axis while the maximum deshielding region lies in the molecular mirror plane parallel to the cyclopentadienyl rings and containing the metal atom, as shown in Figure 1. The extension of these concepts to the $[(arene)Ru(C_5H_5)]^+$ system would allow one to distinguish between the α-CpRu and β-CpRu complexes as long as the assignments of the steroidal protons were securely based. This can best be accomplished by using two-dimensional NMR techniques.[18]

The 500-MHz ^{1}H NMR spectra of the α- and β-$(C_5H_5)Ru$ cationic complexes of estrone 3-methyl ether are shown in Figure 2. Since the ^{13}C NMR spectra of steroidal systems have been extensively studied,[19] it was relatively straightforward to use the two-dimensional ^{1}H–^{13}C shift-correlated experiment as a first step toward obtaining complete proton assignments. These data were used in conjunction with the results of the attached proton test (APT) in which the ^{13}C NMR peaks have positive phase for C and CH_2 environments while CH and CH_3 carbons have negative phase. The proton–proton connectivity

Table I. ^{1}H NMR Chemical Shifts for Estrone 3-Methyl Ether 1 and Its α- and β-$[(C_5H_5)Ru]^+$ Complexes 2a and 2b, Respectively

proton	1	2a	2b
1	7.09	6.47	6.25
2	6.60	6.33	6.20
4	6.54	6.40	6.44
6α	2.79	2.92	3.07
6β	2.84	3.15	3.10
7α	1.40	1.55	1.50
7β	2.00	2.30	2.08
8β	1.60	1.72	1.75
9α	2.20	2.62	2.35
11α	2.38	2.33	2.33
11β	1.45	1.59	1.50
12α	1.48	1.38	1.48
12β	1.85	1.78	1.88
14α	1.55	1.54	1.63
15α	2.05	2.01	2.05
15β	1.67	1.65	1.68
16α	2.09	2.05	2.08
16β	2.45	2.43	2.42
18Me	0.90	0.89	0.97
OMe	3.80	3.82	3.78
C_5H_5		5.46	5.50

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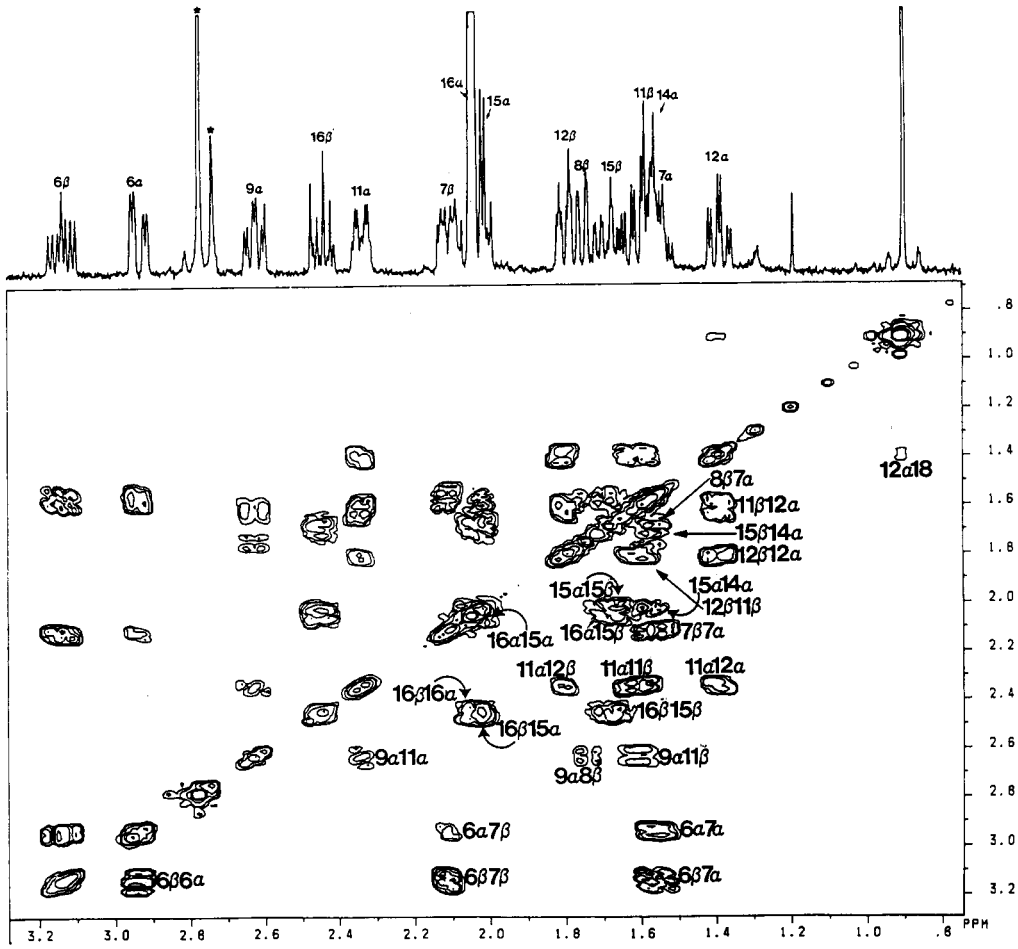

Figure 3. 500-MHz 2-D COSY-45 ^{1}H NMR spectrum of **2a** recorded in acetone-d_6. The matrix has been symmetrized.

pattern was further characterized via the 2-D ^{1}H–^{1}H COSY spectrum in which the conventional 1-dimensional spectrum appears as a contour plot along the diagonal and the off-diagonal contours indicate those protons which are related via scalar coupling interactions. It had been reported that in complex steroidal systems the COSY-90 experiment sometimes yields weak or even nonexistent cross-peaks for proton pairs which would be expected to exhibit strong coupling;[20] this may render some proton assignments rather tentative. However, the COSY-45 experiment does not appear to suffer from this problem, and a typical spectrum (for the α-Ru(C_5H_5) compound **2a**) appears as Figure 3. Any ambiguities as to the positioning of a given proton on the α- or β-face of the steroid were resolved either by an examination of the coupling pattern or via an nOe experiment. The complete ^{1}H and ^{13}C NMR chemical shift assignments are collected in Tables I and II.

There are, of course, obvious changes brought about on the steroidal chemical shifts upon complexation to the (C_5H_5)Ru$^+$ moiety. As is normally seen for π-complexed arenes, the aromatic protons (and carbons) are markedly shielded relative to their resonance positions in the free ligand. On the other hand, one might have anticipated a general shift to high frequency for the protons positioned proximate to the cationic center; this effect is indeed observable. The more useful comparison to make is that between corresponding protons in the α- and β-ruthenium complexes which should be in essentially the same environment except for their geometric disposition with respect to the highly anisotropic organometallic sandwich moiety. In fact, the only major chemical shift difference is found for the 9α proton which absorbs at δ 2.62 in the α-complex but at δ 2.35 in the β-isomer. This particular proton is in the deshielding region of the presumed cone of anisotropy associated with with the (cyclopentadienyl)Ru(arene) unit. In the β-diastereomer, the 9α proton should be clearly in the shielding section of the cone of anisotropy and so the chemical shift of this particular nucleus provides a convenient probe for the site of attachment of the organometallic fragment.

Table II. ^{13}C NMR Chemical Shifts for Estrone 3-Methyl Ether 1 and Its α- and β-[(C_5H_5)Ru]$^+$ Complexes 2a and 2b, Respectively

carbon	1	2a	2b
1	127.30	82.53	81.09
2	112.50	73.41	75.27
3	158.90	134.76	134.19
4	114.70	74.64	78.18
5	138.40	105.50	105.96
6	30.03	27.05	27.96
7	27.30	25.09	26.00
8	39.40	38.95	38.41
9	45.00	44.38	42.50
10	133.20	102.48	101.76
11	26.60	26.09	26.00
12	32.24	32.21	31.85
13	48.30	48.09	47.90
14	51.10	49.97	50.46
15	22.00	21.77	21.05
16	35.90	35.78	35.84
17	219.10	218.58	
18Me	13.80	13.92	14.85
OMe	53.82	57.52	57.54
C_5H_5		81.64	80.94

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Table III. Dihedral Angles (deg) and Vicinal Coupling Constants (Hz) for the Protons at C-6 and C-7

	1		$^3J_{H-H}$	
dihedral angle	θ^a	$^3J_{H-H}$	2a	2b
$6\alpha - 7\alpha$	42	6.2	4.7	7.4
$6\alpha - 7\beta$	68	2.1	≈0.5	2.3
$6\beta - 7\alpha$	161	12.3	11.8	11.5
$6\beta - 7\beta$	50	6.5	5.8	6.7

[a] Dihedral angles are taken from the X-ray crystal structure of estrone 3-methyl ether.[24]

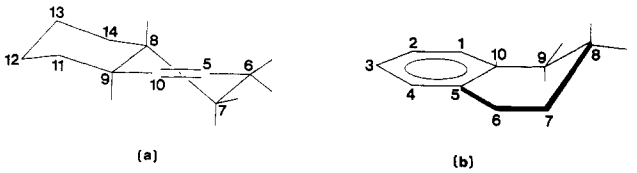

Figure 4. Perspective representations for the A and B rings of 1: (a) in the half-chair and (b) in the sofa conformation.

One might be tempted to place some emphasis on the relative chemical shifts of the 6α and 6β protons in the two isomers as being diagnostic of the position of the $(C_5H_5)Ru$ substituent. However, it is necessary to exercise some caution in this regard since it is well established that estrogenic steroids have considerable conformational flexibility in this region of the molecule.[21] The chemical shifts of the protons bonded to C-6 and C-7 can vary markedly depending upon the conformation of ring B since they can be affected not only by the aromatic ring current of ring A but also by the diamagnetic anisotropy of neighboring fragments such as CpM or $M(CO)_3$. Nevertheless, the H-6 and H-7 protons can yield valuable information about the conformation of the B ring. Despite its limitations,[22] the Karplus equation, which relates vicinal $^3J_{H-H}$ coupling constants and dihedral angles, is a very valuable model for probing molecular geometries.[23] The X-ray crystallographic data on estrone[24] yield the dihedral angles listed in Table III which also contains the corresponding $^3J_{H-H}$ values which were obtained via computer simulation of the 500-MHz spectrum.[20] The corresponding vicinal coupling constants for the ruthenium complexes **2a** and **2b** have been obtained from the spectra shown in Figure 2 and are also listed in Table III. We see in the β-Ru complex that $J_{6\alpha-7\beta}$ and $J_{6\beta-7\beta}$ differ only very slightly from the corresponding values in the free ligand; this suggests that these dihedral angles have not changed dramatically. In contrast, $J_{6\alpha-7\alpha}$ is 7.4 Hz in the β-complex compared to 4.7 Hz in the α-isomer implying that the 6α–7α dihedral angle has opened up in the latter case. Clearly, one would prefer to have crystallographic evidence on this point. Similar effects have been noted previously in a recent study of the α- and β-$Cr(CO)_3$ complexes of methyl *O*-methylpodocarpate where the two diastereomers adopted different B ring conformations.[25]

Distortions of the skeletons of polycyclic systems have been studied in a definitive series of papers by Duax.[21] He has developed very useful criteria for comparing the conformations of estrogenic steroids. One can envisage two extreme situations: firstly, a half-chair conformation in which carbons C(9), C(10), C(5), and C(6) are coplanar while C(8) and C(7) are symmetrically positioned, respectively, above and below this plane (Figure 4a). The second structure (Figure 4b) is the sofa conformer in which five carbons of the B ring are coplanar and C(8) sits on the β side of this plane. The half-chair conformer has local C_2 symmetry about an imaginary axis drawn through the midpoints of the C(5)–C(10) and C(7)–C(8) bonds, while the 8β-sofa conformer has a pseudo mirror plane containing C(5) and C(8). Duax's $\Delta C_s(5)$ and $\Delta C_2(5\text{–}10)$ parameters which measure the deviation of a given conformer from the idealized 8β-sofa and half-chair systems, respectively, are defined as follows:

$$\Delta C_s(8) = \{[(\phi_{5-6} + \phi_{5-10})^2 + (\phi_{6-7} + \phi_{10-9})^2 + (\phi_{7-8} + \phi_{9-8})^2]/3\}^{1/2}$$

$$\Delta C_2(5\text{–}10) = \{[(\phi_{5-6} - \phi_{10-9})^2 + (\phi_{6-7} - \phi_{9-8})^2]/2\}^{1/2}$$

where ϕ_{5-6}, for example, is the dihedral angle within the B ring, i.e., the angle C(10)–C(5)–C(6)–C(7). Thus, for the idealized conformers, the numerical values for these parameters will be zero.

To clarify some of these features it was necessary to obtain X-ray crystallographic data on one of the CpRu

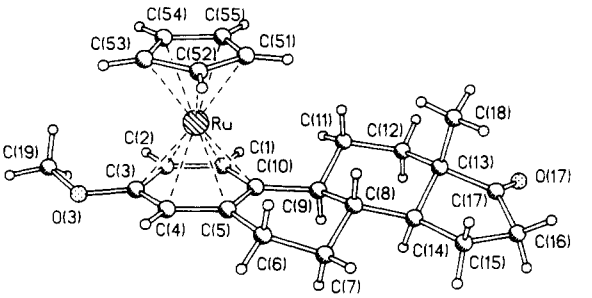

Figure 5. X-ray structure of β-[CpRu(estrone 3-methyl ether)]$^+$ (**2b**).

Table IV. Crystal and Data Collection Parameters for [β-C_5H_5Ru-3-methoxyestrone]PF_6

mol formula	$[(C_{19}H_{24}O_2)Ru(C_5H_5)]^+,PF_6^-$
fw	595.57
cryst system	monoclinic
cryst dim., mm	0.12 × 0.13 × 0.35
space group	$P2_1$
a, Å	8.0717 (7)
b, Å	14.813 (1)
c, Å	10.597 (1)
β, deg	109.93 (2)
V, Å^3	1191.0 (2)
Z	2
D(obsd), g cm^{-3}	1.661
temp, °C	25
μ(Cu Kα), cm^{-1}	6.71
F(000)	604
radiatn Å	1.54178
2θ range, deg	120
data collected	
no. of total data	1989
no. of unique data	1847
no. of obsd data ($F > 3\sigma(F)$)	1837
R_1[a]	0.0251
R_2[b]	0.0325
weighting scheme	$w = 1/[\sigma^2(F_o) + gF_o^2]$ ($g = (0.015)^2$)
final diff Fourier	
highest peak, e/Å^3	0.44
lowest valley, e/Å^3	−0.73
no. of variables	379

[a] $R_1 = (\sum||F_o| - |F_c||/\sum|F_o|)$. [b] $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. $S = [(\sum w\Delta^2)(N_o - N_p)]^{1/2}$.

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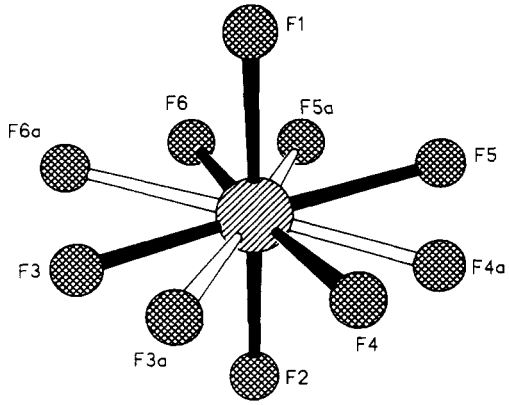

Figure 6. X-ray structure of the disordered PF_6 counterion in **2b**.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

	x	y	z	U(eq)
Ru	1076 (1)	0	9122 (1)	33 (1)
P(1)	-1753 (3)	984 (2)	12678 (2)	61 (1)
F(1)	-3382 (8)	748 (6)	13092 (6)	124 (3)
F(2)	-120 (8)	1204 (7)	12251 (6)	147 (4)
F(3)	-880 (39)	107 (16)	13112 (32)	194 (18)
F(4)	-883 (18)	1398 (16)	14130 (12)	110 (7)
F(5)	-2656 (37)	1961 (13)	12326 (22)	162 (11)
F(6)	-2697 (30)	685 (21)	11239 (14)	142 (11)
F(3A)	-488 (27)	570 (42)	13992 (29)	178 (22)
F(4A)	-1462 (46)	1937 (17)	13113 (49)	163 (23)
F(5A)	-2887 (34)	1310 (29)	11260 (27)	134 (15)
F(6A)	-2053 (28)	-15 (22)	11991 (41)	134 (14)
C(51)	1128 (11)	-1407 (6)	9721 (10)	69 (3)
C(52)	1081 (11)	-856 (7)	10773 (9)	78 (4)
C(53)	2640 (12)	-324 (6)	11187 (8)	75 (3)
C(54)	3587 (10)	-580 (6)	10338 (9)	69 (3)
C(55)	2633 (11)	-1232 (5)	9473 (8)	67 (3)
O(3)	1771 (6)	2170 (3)	9814 (5)	50 (2)
O(17)	-5340 (8)	-2810 (4)	2556 (5)	75 (2)
C(1)	589 (7)	484 (4)	7065 (5)	38 (2)
C(2)	1590 (7)	1141 (4)	7950 (6)	39 (2)
C(3)	954 (8)	1515 (5)	8923 (6)	38 (2)
C(4)	-604 (7)	1180 (4)	9040 (5)	35 (2)
C(5)	-1629 (7)	529 (4)	8154 (5)	33 (2)
C(6)	-3348 (6)	212 (3)	8305 (6)	37 (2)
C(7)	-4620 (7)	-163 (4)	6986 (6)	42 (2)
C(8)	-3708 (7)	-889 (4)	6441 (5)	35 (2)
C(9)	-2178 (7)	-484 (4)	6087 (6)	38 (2)
C(10)	-1050 (6)	169 (4)	7119 (5)	33 (2)
C(11)	-1154 (8)	-1233 (5)	5646 (7)	56 (3)
C(12)	-2351 (9)	-1780 (5)	4463 (7)	58 (3)
C(13)	-3949 (8)	-2139 (5)	4762 (6)	46 (2)
C(14)	-4908 (8)	-1363 (4)	5178 (6)	41 (2)
C(15)	-6688 (8)	-1750 (6)	5096 (8)	57 (3)
C(16)	-7183 (10)	-2358 (6)	3834 (8)	60 (3)
C(17)	-5463 (9)	-2497 (5)	3576 (7)	51 (2)
C(18)	-3470 (13)	-2918 (6)	5785 (9)	69 (4)
C(19)	3509 (12)	2423 (8)	9918 (12)	89 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

complexes of estrone 3-methyl ether. The cation which the NMR data indicated to be the β-isomer gave colorless crystals of its hexafluorophosphate salt which were found to belong to the monoclinic space group $P2_1$. The structure of the cation and the counterion are shown in Figures 5 and 6, while crystal data, atomic coordinates, bond lengths and angles are presented in Tables IV through VII. We note initially that the PF_6 group includes a disorder where the atoms labeled F3a, F4a, F5a, and F6a in Figure 6 have an occupancy of 40%. Nevertheless, our main focus was directed toward the cation which proves conclusively that the CpRu fragment is indeed located on the β-face of the

Table VI. Bond Lengths (Å)

Ru-C(51)	2.175 (7)	Ru-C(52)	2.161 (7)
Ru-C(53)	2.175 (7)	Ru-C(54)	2.174 (7)
Ru-C(55)	2.175 (7)	Ru-C(1)	2.198 (5)
Ru-C(2)	2.218 (6)	Ru-C(3)	2.253 (7)
Ru-C(4)	2.196 (5)	Ru-C(5)	2.215 (5)
Ru-C(10)	2.242 (5)	P(1)-F(1)	1.561 (5)
P(1)-F(2)	1.566 (6)	P(1)-F(3)	1.475 (20)
P(1)-F(4)	1.581 (9)	P(1)-F(5)	1.606 (17)
P(1)-F(6)	1.520 (11)	P(1)-F(3A)	1.545 (17)
P(1)-F(4A)	1.478 (18)	P(1)-F(5A)	1.546 (19)
P(1)-F(6A)	1.631 (24)	C(51)-C(52)	1.392 (13)
C(51)-C(55)	1.353 (12)	C(52)-C(53)	1.422 (12)
C(53)-C(54)	1.417 (12)	C(54)-C(55)	1.373 (11)
O(3)-C(3)	1.358 (8)	O(3)-C(19)	1.419 (8)
O(17)-C(17)	1.211 (8)	C(1)-C(2)	1.400 (8)
C(1)-C(10)	1.422 (7)	C(2)-C(3)	1.413 (8)
C(3)-C(4)	1.397 (8)	C(4)-C(5)	1.402 (8)
C(5)-C(6)	1.524 (7)	C(5)-C(10)	1.434 (7)
C(6)-C(7)	1.529 (8)	C(7)-C(8)	1.524 (8)
C(8)-C(9)	1.530 (7)	C(8)-C(14)	1.529 (8)
C(9)-C(10)	1.510 (8)	C(9)-C(11)	1.548 (8)
C(11)-C(12)	1.529 (9)	C(12)-C(13)	1.525 (9)
C(13)-C(14)	1.533 (9)	C(13)-C(17)	1.518 (9)
C(13)-C(18)	1.539 (10)	C(14)-C(15)	1.522 (8)
C(15)-C(16)	1.548 (10)	C(16)-C(17)	1.518 (10)

Table VII. Bond Angles (deg)

C(52)-Ru-C(51)	37.5 (4)	C(53)-Ru-C(52)	38.3 (3)
C(54)-Ru-C(53)	38.0 (3)	C(55)-Ru-C(51)	36.2 (3)
C(55)-Ru-C(54)	36.8 (3)	C(2)-Ru-C(1)	37.0 (2)
C(3)-Ru-C(1)	66.1 (2)	C(3)-Ru-C(2)	36.8 (2)
C(4)-Ru-C(1)	78.6 (2)	C(4)-Ru-C(2)	66.6 (2)
C(4)-Ru-C(3)	36.6 (2)	C(5)-Ru-C(1)	67.1 (2)
C(5)-Ru-C(2)	79.3 (2)	C(5)-Ru-C(3)	66.4 (2)
C(5)-Ru-C(4)	37.1 (2)	C(10)-Ru-C(1)	37.3 (2)
C(10)-Ru-C(2)	67.3 (2)	C(10)-Ru-C(3)	78.8 (2)
C(10)-Ru-C(4)	67.1 (2)	C(10)-Ru-C(5)	37.5 (2)
F(2)-P(1)-F(1)	179.0 (5)	F(3)-P(1)-F(1)	94.2 (10)
F(3)-P(1)-F(2)	85.0 (10)	F(4)-P(1)-F(1)	87.2 (6)
F(4)-P(1)-F(2)	93.6 (6)	F(4)-P(1)-F(3)	91.8 (11)
F(5)-P(1)-F(1)	84.7 (10)	F(5)-P(1)-F(2)	96.1 (10)
F(5)-P(1)-F(3)	175.5 (12)	F(5)-P(1)-F(4)	83.9 (10)
F(6)-P(1)-F(1)	92.0 (6)	F(6)-P(1)-F(2)	87.4 (6)
F(6)-P(1)-F(3)	94.5 (13)	F(6)-P(1)-F(4)	173.7 (14)
F(6)-P(1)-F(5)	89.8 (12)	F(3A)-P(1)-F(1)	91.1 (8)
F(3A)-P(1)-F(2)	88.9 (8)	F(4A)-P(1)-F(1)	100.7 (11)
F(4A)-P(1)-F(2)	80.3 (11)	F(4A)-P(1)-F(3A)	96.4 (21)
F(5A)-P(1)-F(1)	93.8 (11)	F(5A)-P(1)-F(2)	86.1 (11)
F(5A)-P(1)-F(3A)	171.8 (22)	F(5A)-P(1)-F(4A)	89.1 (19)
F(6A)-P(1)-F(1)	84.9 (9)	F(6A)-P(1)-F(2)	94.1 (9)
F(6A)-P(1)-F(3A)	89.6 (22)	F(6A)-P(1)-F(4A)	171.6 (19)
F(6A)-P(1)-F(5A)	84.3 (15)	C(55)-C(51)-C(52)	108.4 (8)
C(53)-C(52)-C(51)	108.0 (7)	C(54)-C(53)-C(52)	105.5 (7)
C(55)-C(54)-C(53)	108.1 (7)	C(54)-C(55)-C(51)	110.0 (8)
C(19)-O(3)-C(3)	118.4 (5)	C(10)-C(1)-C(2)	122.3 (5)
C(3)-C(2)-C(1)	119.4 (5)	C(2)-C(3)-O(3)	125.3 (5)
C(4)-C(3)-O(3)	115.5 (5)	C(4)-C(3)-C(2)	119.2 (6)
C(5)-C(4)-C(3)	121.9 (5)	C(6)-C(5)-C(4)	119.5 (4)
C(10)-C(5)-C(4)	119.7 (5)	C(10)-C(5)-C(6)	120.8 (5)
C(7)-C(6)-C(5)	111.6 (4)	C(8)-C(7)-C(6)	110.0 (4)
C(9)-C(8)-C(7)	110.5 (5)	C(14)-C(8)-C(7)	114.3 (5)
C(14)-C(8)-C(9)	106.8 (4)	C(10)-C(9)-C(8)	114.3 (4)
C(11)-C(9)-C(8)	110.6 (5)	C(11)-C(9)-C(10)	115.2 (5)
C(5)-C(10)-C(1)	117.3 (5)	C(9)-C(10)-C(1)	121.4 (4)
C(9)-C(10)-C(5)	121.2 (4)	C(12)-C(11)-C(9)	112.0 (5)
C(13)-C(12)-C(11)	111.0 (5)	C(14)-C(13)-C(12)	110.1 (5)
C(17)-C(13)-C(12)	116.7 (5)	C(17)-C(13)-C(14)	99.1 (5)
C(18)-C(13)-C(12)	112.3 (6)	C(18)-C(13)-C(14)	112.9 (6)
C(18)-C(13)-C(17)	105.1 (6)	C(13)-C(14)-C(8)	111.4 (5)
C(15)-C(14)-C(8)	121.8 (5)	C(15)-C(14)-C(13)	105.1 (5)
C(16)-C(15)-C(14)	103.2 (5)	C(17)-C(16)-C(15)	104.6 (6)
C(13)-C(17)-O(17)	125.8 (6)	C(16)-C(17)-O(17)	124.9 (6)
C(16)-C(17)-C(13)	109.3 (6)		

aromatic ring of the steroid. The Ru–Cp contacts average 2.172 (6) Å while the Ru–arene distances are slightly longer at 2.220 (23) Å. These metal–carbon distances may be

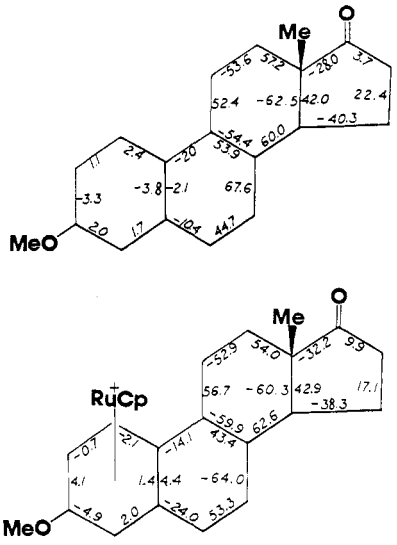

Figure 7. Dihedral angles within the rings of 1 and **2b**.

compared with the values of 2.170 (6) Å (for the cyclopentadienyl carbon–ruthenium bond) and 2.195 (12) Å (for the Ru to arene carbon distances) in $(C_5H_5)Ru(C_6H_5BPh_3)$,[26] which likewise possesses a sandwich structure with a ruthenium positioned between an aryl ring and a cyclopentadienyl ligand. While there does not appear to be a large data base of $[CpRu(arene)]^+$ structures, one could surmise that the significantly longer Ru–arene bonds in the present structure arise because of steric interactions in the steroidal system.

These data now permit a comparison of the structural features of the complex **2b** and of estrone 3-methyl ether itself for which crystallographic results were already available.[24] The dihedral angles within the steroidal ring system are shown in Figure 7 for both free estrone and for **2b**. It is clear that there are conformational differences, notably in the B ring. To emphasize these effects, we show in Figure 8a a view of the crystallographically characterized β-CpRu–estrone 3-methyl ether complex and in Figure 8b a computer-simulated drawing in which the $(C_5H_5)Ru$ fragment has been grafted onto the known structure of the free ligand. It is obvious that in the latter case there would arise an unfavorable steric interaction between the cyclopentadienyl ring and the C(18) methyl group. The unfavorable interactions would place a cyclopentadienyl hydrogen only 1.97 Å from a methyl hydrogen; furthermore, H-8_β would be only 2.35 Å from the Cp ring protons. Evidently, the molecule attempts to alleviate the situation via conformational changes in ring B; thus, in the X-ray crystallographically determined structure, no steroidal hydrogen is less than 2.85 Å from a cyclopentadienyl ring proton.

In terms of Duax's parameters discussed above, the half-chair character of the B ring is little changed; ΔC_2(estrone 3-methyl ether) is 9.4° while ΔC_2(Ru) is 9.9°. In contrast, the sofa character of the B ring is quite different for the two molecules; ΔC_s(estrone 3-methyl ether) is 17.8° while ΔC_s(Ru) has increased to 27.9°. It is apparent that the incorporation of a (cyclopentadienyl)ruthenium cationic fragment into the estrogenic framework not only brings about the anticipated enhancement of the nucleophilic substitution process but also has the effect of causing subtle structural changes which are detectable by X-ray crystallography and by high-field NMR spectroscopy.

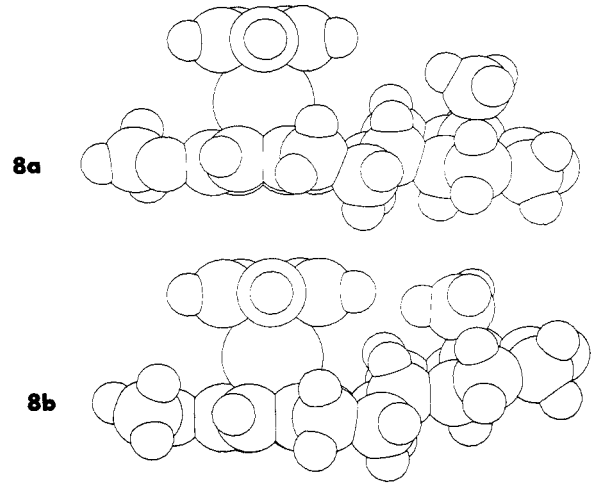

Figure 8. CPK models of β-[CpRu(estrone 3-methyl ether)]$^+$ (**2b**): (a) shows the observed structure which illustrates the torsional relief compared to the structure which would arise by simply grafting CpRu onto the free ligand, as in (b).

Experimental Section

NMR spectra were recorded on a Bruker AM 500 spectrometer. The 500-MHz ^1H and 125.7-MHz ^{13}C spectra were acquired by using a 5-mm dual frequency $^1H/^{13}C$ probe. All spectra were measured in acetone-d_6 at 300 K, and chemical shifts are reported relative to tetramethylsilane. Proton spectra were acquired in 16 scans over a 3000 Hz spectral width in 32K data points, processed by using Gaussian multiplication for line enhancement and zero filled to 64K before transformation.

Homonuclear chemical shift correlation (COSY) experiments were carried out by using the pulse sequence: delay – $(\pi/2, {}^1H)$ – t_1 – $(\pi/4, {}^1H)$ – acquisition. Pulses were phase cycled according to ref 27. A 2-s relaxation delay was used: the $\pi/2$ pulse was 18 μs. The spectra were acquired in eight scans for each of 256 FID's which contained 1024 data points in f_2. The data were zero filled once in the t_2 domain and yielded a 512 × 512 matrix after transformation. The transformation matrix was symmetrized.

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. A 2-s relaxation delay was used, and the delay times $\Delta_1 = 1/2J$ and $\Delta_2 = 1/4J$ were calculated from a compromise value of $^1J(C,H)$ = 125 Hz. The $\pi/2$, ^1H pulse was 18 μs and $\pi/2$, ^{13}C pulse was 7.3 μs. The spectral width in the t_2(carbon) domain was 17 857 Hz (140 ppm) and in the t_1(proton) domain was 3000 Hz. The spectra were acquired containing 4K data points in f_2 for each of 256 FID's. Zero filling twice in f_2 followed by 2-D transformation created a 2K × 512 data matrix. Gaussian enhancement of the data was applied.

Synthesis of (η^6-Estrone-3-methyl ether)(η^5-cyclopentadienyl)ruthenium(II) Hexafluorophosphate (2). A solution of estrone 3-methyl ether (569 mg, 2.0 mmol) in 35 mL of 1,2 dichloroethane was degassed for 10 min with nitrogen, and $[CpRu(CH_3CN)_3]PF_6$[28] (668 mg, 1.54 mmol) was added. After the mixture was heated for 15 h at 40 °C under nitrogen, the solvent was removed by rotary evaporation and the residue was washed with ether (4 × 15 mL) to remove the unreacted estrone 3-methyl ether. The solid residue was redissolved in acetone and decolorized with charcoal. After concentration of the acetone solution to about 3 mL, ether was added to precipitate 488 mg (0.82 mg, 53% yield) of a mixture of the α- and β-stereoisomers in a 7:3 ratio (the ratio of the two isomers was determined by ^1H NMR; the integration of the two Cp signals reveals the ratio); mp 153–157 °C. Anal. Calcd for $C_{24}H_{29}O_2RuPF_6$: C, 48.40; H, 4.91. Found: C, 48.40; H, 5.03.

The β-isomer was found to be much less soluble in acetone than the α-isomer. The separation of the two isomers was achieved

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by dissolving the mixture in a minimum amount of acetone, adding a few drops of ether, and allowing the clear solution to stand overnight at room temperature. The crystals were washed with acetone/ether (8:3) to remove the α-isomer. The pure β-isomer, 95 mg, was obtained [mp 288–290 °C; IR (KBr) ν_{CO} 1752 cm^{-1}]. The pure α-isomer, 101 mg, was obtained [mp 155–157 °C: IR (KBr) ν_{CO} 1750 cm^{-1}] by repeating the above process several times.

When the above synthesis was carried out in 70 mL of 1,2-dichloroethane, the α and β ratio was the same, i.e., 7:3.

X-ray Structure Determination of 2b. An automated Nicolet R3m diffractometer with incident beam graphite monochromator and Cu Kα X-rays (λ = 1.541 78 Å) was used to collect the intensities of 1989 reflections [2θ(max) = 120.0°]. Of these, 1847 were unique (nonredundant) data and 1837 were considered observed [$F_o > 3\sigma(F_o)$]. Empirical absorption corrections were estimated from psi-scan observations on 20 selected reflections; minimum and maximum transmission coefficients were 0.51 and 0.98, respectively. The structure was solved by direct methods and refined by using full-matrix least-squares methods contained in the program package SHELXTL.[29] The quantity $\sum w(F_o - F_c)^2$ was minimized, where $w = 1/[\sigma^2(F_o + gF_o^2]$ ($g = (0.015)^2$). Final refinement with 379 variables (H atoms isotropic, all others anisotropic) yields $R_1 = 0.0251$, $R_2 = 0.0325$, and $S = [(\sum w\Delta^2)/(N_o - N_p)]^{1/2}$. Maximal ripples in the final Fourier difference map were 0.44 and −0.73 e $Å^{-3}$.

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Supplementary Material Available: Tables of anisotropic temperature factors and H-atom coordinates (2 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Formation of Alkenyl Ketone Complexes and of Dimeric α,β-Butenolides by Sequential Insertion of Phenylacetylene and Carbon Monoxide into Nickel–Acyl Bonds. X-ray Structures of $Ni[C(Ph)=C(H)(COCH_2SiMe_3)]Cl(PMe_3)_2$ and $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$

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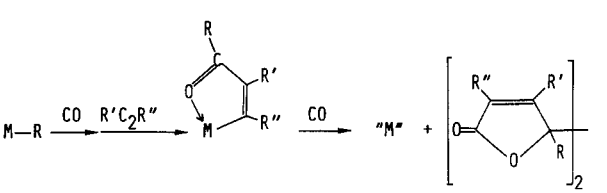
The insertion of PhC≡CH into the nickel–carbon bond of the acyls *trans*-$Ni(COR)Cl(PMe_3)_2$ is highly regio- and stereoselective and provides goods yields of *trans*-(*Z*)-$Ni[C(Ph)=C(H)(COR)]Cl(PMe_3)_2$ (R = CH_3, **1a**; R = CH_2SiMe_3, **1b**; R = CH_2CMe_3, **1c**; R = $CH_2C_6H_4$-*o*-Me, **1d**; R = CH_2CMe_2Ph, **1e**). The nickel center in these complexes is in a five-coordinate distorted square-pyramidal environment, as demonstrated by an X-ray study carried out with the CH_2SiMe_3 derivative **1b**. The neophyl complex **2e** undergoes a reversible 1,2 trimethylphosphine shift and rearranges to the nickelacyclopropane complex $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$ (**2**) whose structure has also been determined by X-ray crystallography. Complex **1b** is monoclinic of space group $P2_1/n$, while **2** is orthorhombic of space group *Pbca*. **1b** has unit cell parameters $a = 12.532$ (8) Å, $b = 14.099$ (1) Å, $c = 14.36$ (1) Å, $\beta = 98.51$ (6)°, and D(calcd) = 1.23 g cm^{-3} for $Z = 4$. Corresponding values for **2** are $a = 20.638$ (5) Å, $b = 20.09$ (1) Å, $c = 12.913$ (5) Å, and D(calcd) = 1.26 g cm^{-3} for $Z = 8$. The keto vinyl complexes **1** react smoothly with CO (20 °C, 1 atm) with formation of dimers of γ-but-2-enolactone, **3**, in good yields. Formation of these dimeric α,β-butenolides can be achieved in a one-pot synthesis, starting from the alkyls $NiCl(R)(PMe_3)_2$, by successive insertion of CO, PhC≡CH, and CO.

At variance with the large number of investigations concerning the addition of M–R bonds to carbon monoxide,[2] studies related to the insertion of alkynes into transition metal–alkyl bonds have been explored less.[3]

Scheme I



Sequential insertion of carbon monoxide and an alkyne is an attractive reaction of potential importance for the synthesis of organic molecules.[4] Very often, the resulting

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(2) See, for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA 1987.

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