idence for $\pi$-electron donation from $Mo(OPr\text{-}i)_2$ to the antibonding orbitals of the bpy ligands. The extent of this back-donation can be calculated quantitatively from the bpy vibrational frequencies, but justification of such a calculation is beyond the scope of this communication. Qualitatively, the RR frequencies are consistent with a net negative charge of approximately 0.5 $e^-$ in the lowest $\pi^*$ orbitals of each bpy in $Mo(OPr\text{-}i)_2(bpy)_2$.

We conclude that the $Mo(OR)_2$ moiety is a most unusually powerful $\pi$ donor, even to ligands like 2,2′-bipyridine which do not normally act as $\pi$-acceptor ligands in the ground state. The only other transition-metal complexes which are perhaps analogous to $Mo(OPr\text{-}i)_2(bpy)_2$ are the 1,4-diimine adducts of $Cp_2Ti$ and $Cp_2Zr$, studied by Stucky and his co-workers.[13,14]

**Acknowledgment.** We thank the National Science Foundation, donors of the Petroleum Research Fund, administered by the American Chemical Society, and Marshal H. Wrubel Computing Center for support at Indiana University and the National Science Foundation and Robert A. Welch Foundation for support at the University of Texas.

**Supplementary Material Available:** Fractional coordinates and isotropic and anisotropic thermal parameters for $Mo(OPr\text{-}i)_2(bpy)_2$ and 2,2′-bipyridine (5 pages). Ordering information is given on any current masthead page.

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[13] McPherson, A. M.; Fieselmann, B. F.; Lichtenberger, D. L.; McPherson, G. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 3425.

[14] Corbin, D. R.; Willis, W. S.; Duesler, E. N.; Stucky, G. D. *J. Am. Chem. Soc.* **1980**, *102*, 5969.

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## A Semichelating Metal-$\beta$-Diketonate Complex

A. R. Siedle* and R. A. Newmark

*3M Central Research Laboratories*
*St. Paul, Minnesota 55101*

L. H. Pignolet

*Department of Chemistry, University of Minnesota*
*Minneapolis, Minnesota 55455*

*Received January 22, 1981*

Comprehensive investigations of the isomerization process in octahedral metal-$\beta$-diketone complexes have revealed two limiting mechanistic pathways which may be distinguished by the effective coordination number of the metal in the transition state. They are (1) twist mechanisms, in which chemical bonds are not broken, and (2) bond rupture pathways which lead to idealized square-pyramidal or trigonal-bipyramidal intermediates with "dangling" axial or equatorial ligands.[1-3] We wish to report the synthesis of a new compound whose structure and NMR spectra reveal novel bonding features like those proposed for the dangling ligand in bond rupture isomerizations or, alternatively, in substitution processes in square planar complexes.

Reaction of the tridentate phosphine $Ph_2PC_2H_4P(Ph)C_2H_4PPh_2$ (triphos) with palladium bis(hexafluoroacetylacetonate) [$Pd(F_6acac)_2$] in benzene affords the 1:1 adduct (triphos)$Pd(F_6acac)_2$ (**1**), mp 192 °C; $^{31}P$ NMR $\delta$ 108.2 (d) and 48.6 (t, $J_{PP}$ = 9.5 Hz).[4] Crystals suitable for X-ray diffraction experiments were grown by slow evaporation of an ethanol solution.[5]

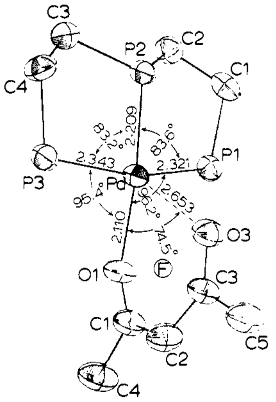

**Figure 1.** Coordination core of (triphos)$Pd(F_6acac)_2^+$.

The solid-state structure of **1** contains two types of hexafluoroacetylacetonate groups. One is not bonded to the metal and corresponds to ionic $F_6$ $acac^-$. The other is attached to palladium by a normal 2.110 (5) Å Pd–O bond as shown in Figure 1, which depicts the coordination core of the metal. The other three coordination sites are occupied by phosphorus atoms from the triphos. The palladium atom is displaced by 0.22 Å in the direction of O(3) from the weighted least-squares plane containing P(1), P(2), P(3), and O(1). A novel feature of the bonding in (triphos)$Pd(F_6acac)_2$ involves O(3), the other terminus of the coordinated $F_6acac$ group. This ligand, which is planar within experimental error, is positioned so that its plane makes a dihedral angle of 85.4° with the $P_3OPd$ plane. In this conformation, O(3) lies above the palladium atom in an axial position. The resulting Pd–O contact, 2.653 (6) Å, is rather long, and it presumably represents a weakly bonding interaction so that the overall coordination geometry is described as distorted square pyramidal. The principal distortion is due to the small "bite" angle of the $F_6acac$ ligand [O(1)–Pd–O(3), 74.5 (4)°] which places O(3) slightly off of the ideal axial position. The O(3)–Pd–P equatorial angles reflect this: O(3)–Pd–P(1), 97.5; O(3)–Pd–P(2), 113.8; O(3)–Pd–P(2), 97.4°. The weakly bonding axial Pd–O interaction is much shorter than the 3.1-Å axial Pd–O contact observed in $Pd(F_6acac)_2\cdot(4\text{-}ClC_5H_4N)_4$.[6] A much less drastic distortion in another $F_6acac$ complex, (bpy)$Cu(F_6acac)_2$, has been proposed to arise from a Jahn–Teller effect, but the longer Cu–O bond was 2.296 (4) Å.[7]

Variable-temperature NMR spectroscopy revealed two dynamic processes in **1**. The $^{19}F$ NMR spectrum of (triphos)$Pd(F_6acac)_2$ in $CD_2Cl_2$ at −64 °C demonstrated three singlets in a 1:2:1 ratio at 75.44, 76.08, and 77.24 ppm. The center field resonance is assigned, on the basis of its chemical shift and relative intensity, to the ionic $F_6acac$. On warming, these three signals coalesced into a single broad peak. These data indicate that there is a facile exchange between ionic and coordinated $F_6acac$; $\Delta H_{act}$ for this process was found to be 6 kcal $mol^{-1}$ and $\Delta S_{act}$ to be −26 eu.[4]

The coordinated $F_6acac$ ligand is itself fluxional. Variable-temperature $^{19}F$ NMR spectra of [(triphos)$Pd(F_6acac)$]$BPh_4$ (**2**) prepared by metathesis of **1** with sodium tetraphenylborate in methanol, showed that the two types of $CF_3$ groups rapidly interconvert on the NMR time scale. The limiting low-temperature spectrum, obtained at −11 °C, showed two fluorine resonances at 75.75 and 77.86 ppm. The activation enthalpy for this second process, measured for a $5 \times 10^{-2}$ M solution in 1,2-dichloroethane, was 8.1 ± 1 kcal $mol^{-1}$ with $\Delta S_{act}$ −21 ± 3 eu. Since the reaction rates, as reflected by the NMR line shapes, are the same at both $5 \times 10^{-2}$ and $7 \times 10^{-3}$ M concentrations, it is probable that the exchange is intramolecular.

Rapid exchange of the two inequivalent ends of an acetylacetonate group has been observed, for example, in the silicon enol complexes $R_3Si(acac)$.[8] In sulfur chelates, fluxional behavior

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1967, pp 300–334.

[2] N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).

[3] L. H. Pignolet, *Top. Curr. Chem.*, **56**, 93 (1975).

[4] $^{31}P$ and $^{19}F$ NMR chemical shifts are with respect to external 85% $H_3PO_4$ or internal $CFCl_3$.

[5] X-ray diffraction data: crystal system orthorhombic; space group $Pna2_1$; $a$ = 31.120 (7), $b$ = 14.690 (3), $c$ = 10.037 (2) Å; V = 4589 Å$^3$; Z = 4; density = 1.527 g cm$^{23}$; diffractometer = Enraf–Nonius CAD 4; radiation = graphite monochromatized Mo K$\alpha$; scan range $0° \le 2\theta \le 50°$; reflections collected = 4765 total unique, 3330 observed with $F_o^2 > 2.0\sigma(F_o^2)$; $R$ = 0.049 and $R_W$ = 0.066. by full-matrix least-squares refinement.

[6] A. R. Siedle and L. H. Pignolet, submitted for publication.

[7] M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Am. Chem. Soc.*, **91**, 1859 (1969).

[8] T. J. Pinnavaia, W. T. Collins, and J. L. Howe, *J. Am. Chem. Soc.*, *92*, 4544 (1970).

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has been observed in Ni(SacSac)(PEt$_3$)Cl,[9] and the solid-state structure of Zn[S$_2$CN(CH$_3$)$_2$]$_3^-$ exhibits four short and two long zinc–sulfur bonds with $d(\text{Zn–S})_{\text{av}}$ = 2.31 and 3.13 Å, respectively.[10] In the present case, fast F$_6$acac exchange and rearrangement in **1** and **2** may be facilitated by the electron-withdrawing effect of the CF$_3$ groups.

We refer to the hexafluoroacetylacetonate bonding mode in **1**, which features one short and one long metal–oxygen separation, as semichelating and suggest that it is an attractive model for transition states in some substitution or isomerization reactions of metal chelates.

**Supplementary Material Available:** A listing of the positional and thermal parameters derived from the crystallographic analysis (3 pages). Ordering information is given on any current masthead page.

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(9) J. P. Fackler and R. F. Masters, *Inorg. Chim. Acta*, **39**, 111 (1980). SacSac refers to pentane-2,4-dithionato(1–).

(10) C. C. Ashworth, N. A. Bailey, M. Johnson, J. A. McCleverty, N. Morrison, and B. Tabbiner, *J. Chem. Soc., Chem. Commun.* 743 (1976).

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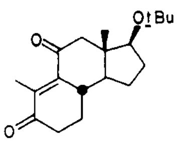
## A New Route to 11-Oxygenated Steroids

Gilbert Stork,* G. Clark, and Christopher S. Shiner

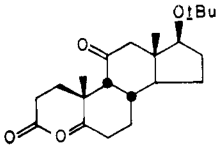
*Department of Chemistry, Columbia University*
*New York, New York 10027*

*Received March 9, 1981*

The steroid structure is an extremely useful target in the development of new regio- and stereochemically controlled synthetic methods.[1] For that reason, and because of their continued importance, we have been particularly interested in 11-oxygenated steroids. We have recently described[2] the transformation **1** → **2** → **3** which served to demonstrate the feasibility and stereochemistry of the kinetic enolate trapping method[3] in the reductive alkylation of enediones of type **1**.



1



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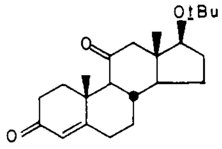
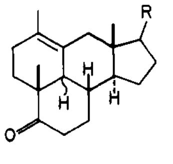


3

The usefulness of triones such as **2** as precursors to the Δ$^4$-3,11-diketo system raised the question whether the particular methylcyclohexene **4**, another potential precursor of the trione **2**, might not be readily accessible via the [4 + 2] cycloaddition of a trienone like **5**.



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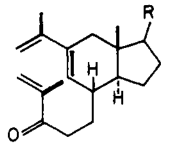
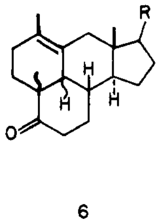


5

The [4 + 2] cycloaddition of **5** can formally generate four diastereoisomers (cf. **6**). Only two of these are likely, however, because the transition state for approach of the enone chain from the underneath (α) side of the indane system is clearly favored. Of the resulting two possible cis B/C products the major one should have the correct β orientation of the pro-C-10 methyl group, as a result of what appears to be a very reasonable endo transition state. It is therefore an attractive possibility that the major product from the cyclization of **5** would have the desirable structure shown in **4**.

We now demonstrate the effectiveness of this approach starting with the keto acid **7**[4] which can thus be transformed into the desired 11-ketotestosterone derivative **15** in just five steps.



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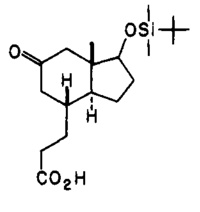
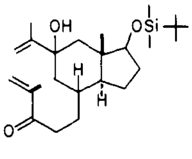


7

Addition of an excess of lithium isopropenyl[5] to **7** (4 equiv in ether, –78 → 25 °C, quenched with acetic acid in ethyl acetate) gave, after purification on silica, the enone alcohol **8** in >90% yield [NMR δ 1.0 (quaternary CH$_3$), 1.77, 1.36 (allylic methyls), 4.8, 5.02 (CH$_3$C=CH$_2$), 5.75, 5.85 (H$_2$C=C–C=O)]. Dehydration of **8** (Burgess' salt[6], tetrahydrofuran, room temperature) gave largely the conjugated diene **9** (NMR δ 5.65 for the starred vinyl hydrogen) with the new double bond parallel to the ring junction, as expected. The minor isomer (**10**) from the dehydration was noticeable by the position of the starred vinyl hydrogen at δ 6.05. The small quantity of isomeric diene does not undergo the cycloaddition reaction, after which it is most easily removed.



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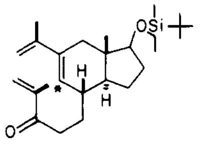

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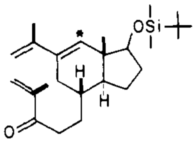

10

Various conditions were tried for the [4 + 2] cycloaddition. It was possible to effect both dehydration and cycloaddition simultaneously by simple heating of the enone alcohol **8** with iodine (1 mg/mL) in dimethoxyethane to ~70 °C. Under these conditions, however, the ratio in favor of the desired endo isomer was only ~1.5:1. It was eventually found that the desired adduct **11** could be obtained as the major product by conducting the reaction at –78 °C in methylene chloride in the presence of 2 equiv of trifluoroacetic acid. Quenching with triethylamine after 4 h gave, after silica gel purification, the endo–exo mixture of cyclization products **11** and **12** in ~70% yield. The ratio of desired endo to exo isomer was 94:6, as determined by MPLC. The two quaternary methyl groups of **11** occur at δ 0.94 and 1.06, while resonances occur at δ.72 and 1.0 in **12**.

Ozonolysis of **12** (1:1 methanol–methylene chloride –78 °C, decomposition with triphenylphosphine) now led to the triketone

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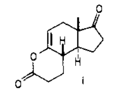
(1) For the most impressive illustration see: Johnson, W. S.; Brinkmeyer, R. S.; Kapoor, V. M.; Yarnell, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 8341.

(2) Stork, G.; Logusch, W. E. *J. Am. Chem. Soc.* **1980**, *102*, 1219.

(3) Stork, G.; Rosen, P.; Goldman, N.; Coombs, R. V.; Tsuji, J. *J. Am. Chem. Soc.* **1965**, *87*, 275.

(4) Since the purpose at this stage was to examine the possibility of the **7** → **15** transformation, the hydrindanone *7* was simply made by moving the carbonyl of the steroid intermediate *i* which is readily available in optically active form. The transformation, while not a particularly satisfactory way to make indanones of type **7** proved of some interest and is detailed elsewhere.



i

(5) Made by adding 2-bromopropene slowly to a suspension of lithium (2% sodium) dispersion in ether: See: Smith W. N. *J. Organomet. Chem.* **1974**, *82*, 7. The various products described here had unambiguous spectral characteristics. The structures are, in any event, made unequivocal by their further transformations.

(6) Burgess, E. M.; Penton, H. R.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26.

0002-7863/81/1503-4948$01.25/0