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Reduction of Aldehydes and Ketones by Transition Metal Hydrides. 3.[1] Reduction of β-Diketones by *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ with Formation of Tungsten(0) β-Diketonates

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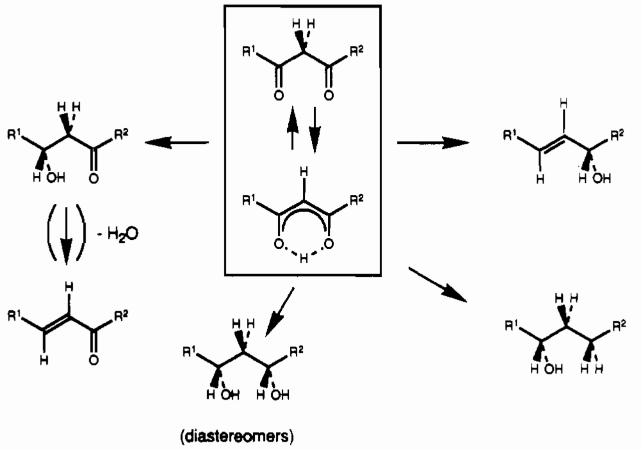
The tungsten hydride *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ (**1**) reduces a wide variety of β-diketones selectively to β-hydroxy ketones in most cases, with concomitant formation of *trans*-W(β-diketonate)(CO)(NO)$(PMe_3)_2$ (**2**). For reactions of **1** with those β-diketones that contain a CF_3 group and which were started at low temperature, intermediates could be detected by NMR, which were identified as the primary insertion product (**3**) existing as an unique mixture of keto and enol tautomers. Those β-diketones that contain two different β-substituents afford a mixture of two, extremely slowly exchanging (but accelerated by the addition of PMe_3) isomers **2xy** and **2yx**, differing only by the relative positions of the CO and NO ligands. In solution, the isomer ratios **2xy**:**2yx** are balanced by the difference in electron-withdrawing properties of the two β-substituents in combination with the difference in π-acceptor capabilities of the CO and NO ligands. In some cases these isomers were found to interconvert in the *solid state* as well, a conversion that seems to be catalyzed by CO. The subtle influence of the β-substituents on a number of spectroscopic parameters in **2** (IR, ^1H, ^{13}C, ^{19}F, ^{31}P NMR, UV/vis, MS) was studied in detail. An X-ray structure of one representative of the series, **2ac**, was determined. Crystals are monoclinic $P2_1/c$, with a = 12.705 (5) Å, b = 9.757 (4) Å, c = 16.774 (6) Å, β = 99.22 (3)°, and Z = 4 with R = 0.0379 and R_w = 0.0375 for 2736 observed reflections. The octahedral molecule contains a plane in which the β-diketonate ligand has one β-substituent (CF_3) quasi trans to NO and the other (Me) trans to CO.

Introduction

The reduction of β-diketones[2] by metallic hydrides may lead to a variety of products (Scheme I).[3] The primary reduction products are β-hydroxy ketones, but normally the reaction is difficult to stop at this stage, since further reduction usually occurs affording 1,3-diols or (unsaturated) alcohols. Product distribution depends on a number of factors like solvent, temperature, reducing agent ($NaBH_4$ and $LiAlH_4$ are frequently used), and the substituents of the β-diketone. The study of these factors is complicated by the fact that β-diketones are highly dynamic compounds. In solution they may consist of several interchanging keto and enol conformers.[4] Therefore, the two β-substituents (R^1 and R^2 in Scheme I) have a major impact on the selectivity and degree of reduction.

Scheme I. Possible Reduction Products of β-Diketones[3]



We have shown that the tungsten(0) hydride *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ (**1**) can reduce a variety of aldehydes and ketones.[1] Generally, these reductions are considerably accelerated by acids, as far as they do not react with the metal hydride itself.[5] This has been explained by hydrogen bridge formation between the ketonic O atom and the acid H atom, thus enhancing the electrophilicity of the ketonic C atom and facilitating nucleophilic attack by the hydride atom. This is elegantly demonstrated as one compares the facile insertion reaction between **1** and the intramolecularly activated salicylaldehyde with the rather reluctant reaction between **1** and benzaldehyde.[1a] We therefore argued that β-diketones, in their cis enol form, might be susceptible to reduction by **1**, due to a similar form of intramolecular activation. We therefore set out to investigate the reaction of **1** with a number of β-diketones,[2] in order to study the intimate steps of their reduction and selectivity thereby in greater detail.

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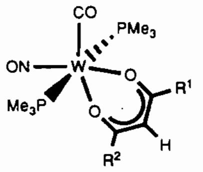
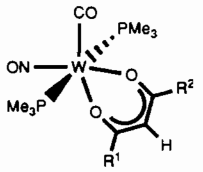
Table I. Compound Numbering System for **2**[a] and Reaction Conditions and Yields for the Formation of **2** from **1**



2xy



2yx

cmpd[a]	R^1	R^2	reacn time and temp	yield (%)
2aa	CF_3	CF_3	s at 20 °C	95
2ab/2ba	CF_3	Ph	1 h at 50 °C	80
2ac/2ca	CF_3	Me	min at 20 °C	90[b]
2ae/2ea	CF_3	OEt	3 h at 20 °C	90
2bb	Ph	Ph	3 d at 50 °C	85
2bc/2cb	Ph	Me	3 d at 50 °C	90[b]
2be/2eb	Ph	OEt	8 d at 50 °C	75
2cc	Me	Me	2 d at 50 °C	75
2cd/2dc	Me	OMe	6 d at 50 °C	60
2ff	tBu	tBu	9 d at 50 °C	55

[a] Compound indexes are grouped in such a way that **a** refers to a CF_3 group, **b** = Ph, **c** = Me, **d** = OMe, **e** = OEt, and **f** = tBu. The combination **2xy** refers to an arrangement whereby group R^1 is trans to NO and R^2 trans to CO; consequently, its isomer **2yx** has R^1 trans to CO and R^2 trans to NO. [b] The isomers were separated by column chromatography.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen, by conventional Schlenk techniques. All of the described reaction products, however, could be handled in air. Solvents were dried and freshly distilled before use. *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ (**1**) was prepared as described previously.[6] All β-diketones were commercially available (Fluka AG or Aldrich) and were used as obtained. Elemental analyses were carried out by the Analytical Department of the Organic Laboratory of Zürich University. IR spectra were recorded as a hexane solution on a Biorad FTS-45 instrument. Mass spectra were run on a Finnigan MAT-8230 mass spectrometer with a 70-eV electron-impact ion source; the major peaks given are based on ^{184}W. UV/vis spectra were recorded on a Varian Cary 2300 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a Varian Gemini-200 spectrometer operating at 200 and 50.3 MHz, respectively, ^{31}P NMR spectra on a Varian XL-200 at 81 MHz or on a Gemini-300 at 121 MHz, and ^{19}F NMR spectra on a Varian Gemini-300 at 282 MHz.

Syntheses of the Tungsten β-Diketonates 2xy. The preparations of complexes **2xy** were similar in all cases except for **2dd** and **2ee**. Thus, to a solution of **1** (ca 0.13 g, 0.3 mmol) in toluene (10 mL) was added slightly more than 2 equiv of the appropriate β-diketone. The reaction was monitored by IR (reaction times and temperatures are listed in Table I), and after completion toluene was removed in vacuo. The residue was thoroughly washed a few times with water in order to remove most of the organic material and dried in vacuo. The residue was then either washed with, or recrystallized from, hexane. Yields are given in Table I.

Compounds **2ab/2ba**, **2ae/2ea**, **2be/2eb**, and **2cd/2dc** were isolated as a mixture of two isomers. The isomer mixtures **2ac/2ca** and **2bc/2cb** were separated by column chromatography on silica with diethyl ether/hexane (2:1) as an eluents, the isomers **2ac** and **2bc** running ca 20% faster as their counterparts **2ca** and **2cb**, respectively. Diffraction-quality crystals of **2ac** were obtained by slow cooling of a saturated solution of this compound in hexane from +20 to -80 °C within 2 d.

Combustion analyses of **2aa**, **2ab/2ba**, **2ac/2ca**, and **2ad/2da** were not performed due to the vulnerability of our in-house instruments to fluorine. Anal. Calcd (found) for $C_{22}H_{29}NO_4P_2W$ (**2bb**): C, 42.82 (42.81); H, 4.85 (4.74). Calcd (found) for $C_{17}H_{27}NO_4P_2W$ (**2bc/2cb**): C, 36.97 (36.78); H, 5.18 (4.90). Calcd (found) for $C_{18}H_{29}NO_5P_2W$ (**2be/2eb**): C, 37.18 (36.94); H, 5.13 (4.99). Calcd (found) for $C_{12}H_{25}NO_4P_2W$ (**2cc**): C, 28.93 (29.23); H, 5.13 (5.11). Calcd (found) for $C_{12}H_{25}NO_5P_2W$ (**2cd/2dc**): C, 28.50 (28.31); H, 5.01 (4.95). Calcd (found) for $C_{18}H_{37}NO_4P_2W$ (**2ff**): C, 37.52 (37.45); H, 6.69 (6.46).

Syntheses of 2dd and 2ee. Since the dimethyl and diethyl esters of malonic acid did not react with **1**, an alternative pathway was pursued. Thus, a mixture of [*cis,mer*-$W(CO)_3(NO)(PMe_3)_2$][BF_4][6] (0.61 g, 1.1 mmol) and a slight excess of $NaCH(CO_2R)_2$ (R = Me, Et) (prepared from NaOR and $CH_2(CO_2R)_2$ in ROH) in 20 mL of THF was refluxed until an almost clear orange solution developed (ca. 1 h). The solvent was then removed in vacuo and the residue extracted with hexane. Concentrating and chilling of the combined extracts afforded **2dd** and **2ee** in 30–40% yield. Anal. Calcd (found) for $C_{12}H_{25}NO_6P_2W$ (**2dd**): C, 27.60 (27.45); H, 4.81 (4.80). Calcd (found) for $C_{14}H_{29}NO_6P_2W$ (**2ee**): C, 29.81 (30.40); H, 5.65 (5.28).

Table II. Crystal Data for $W(CO)(NO)PMe_3)_2[CF_3C(O)CHC(O)Me]$ (**2ac**)

formula	$C_{12}H_{22}F_3NO_4P_2W$	*Z*	4
mol wt	547.1	d_c/g·cm^{-3}	1.770
cryst system	monoclinic	μ/cm^{-1} (Mo Kα)	59.40
space group	$P2_1/c$	temp/K	238
a/Å	12.705 (5)	no. of reflcns	3131
b/Å	9.757 (4)	no. of unique reflctns	2783
c/Å	16.774 (6)	no. of obsd reflcns [$F > 6\sigma(F)$]	2736
β/deg	99.22 (3)	no. of variables	211
V/Å^3	2052.5 (14)	R, R_w values[a]	0.0379, 0.0375

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = \sum(\|F_o| - |F_c\|w^{1/2})/\sum(|F_o|w^{-1/2})$ with $w = \sigma^{-2}(F_o)$.

Table III. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for the Non-Hydrogen Atoms of **2ac**

atom	x/a	y/a	z/a	U(eq)[a]
W	0.2662 (1)	0.2399 (1)	0.2429 (1)	0.046 (1)
P(1)	0.3438 (2)	0.0414 (2)	0.1791 (1)	0.058 (1)
P(2)	0.1808 (3)	0.4450 (2)	0.2942 (1)	0.056 (1)
F(1)	–0.0724 (6)	0.2975 (8)	0.0734 (4)	0.105 (3)
F(2)	–0.0081 (5)	0.1345 (6)	0.0155 (4)	0.097 (3)
F(3)	–0.0138 (5)	0.3310 (7)	–0.0366 (3)	0.106 (3)
O(1)	0.3288 (5)	0.3676 (6)	0.1577 (3)	0.055 (2)
O(2)	0.1300 (5)	0.2304 (5)	0.1490 (3)	0.050 (2)
O(3)	0.1616 (7)	0.0374 (8)	0.3487 (4)	0.101 (4)
O(4)	0.4497 (6)	0.2431 (7)	0.3823 (4)	0.082 (3)
N	0.3752 (6)	0.2445 (7)	0.3250 (4)	0.054 (3)
C	0.1990 (8)	0.1156 (9)	0.3079 (5)	0.056 (4)
C(1)	0.3582 (9)	0.496 (1)	0.0415 (6)	0.090 (5)
C(2)	0.0062 (9)	0.2650 (9)	0.0333 (5)	0.059 (4)
C(3)	0.2892 (9)	0.4064 (8)	0.0871 (5)	0.059 (4)
C(4)	0.1854 (8)	0.3724 (8)	0.0484 (4)	0.053 (4)
C(5)	0.1161 (8)	0.2922 (8)	0.0809 (4)	0.047 (4)
C(6)	0.042 (1)	0.429 (1)	0.2951 (7)	0.105 (7)
C(7)	0.189 (1)	0.604 (1)	0.2427 (8)	0.121 (7)
C(8)	0.234 (1)	0.484 (1)	0.3989 (6)	0.102 (6)
C(9)	0.4144 (9)	–0.078 (1)	0.2519 (7)	0.099 (6)
C(10)	0.4391 (9)	0.080 (1)	0.1115 (8)	0.100 (6)
C(11)	0.2485 (9)	–0.071 (1)	0.1175 (6)	0.080 (5)

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

An isomer mixture of **2ac/2ca** was also prepared in this way; yield ca. 20%.

Mass spectra of all compounds have been measured and may be obtained as supplementary material (Table S3).

X-ray Analysis of 2ac. A dark red crystal of dimensions 0.4 × 0.5 × 0.5 mm was sealed in a thin-walled glass capillary and mounted on a Siemens P3 diffractometer equipped with a graphite-monochromated Mo Kα X-ray beam. Cell constants and the orientation matrix were obtained and refined from the settings of 34 centered reflections of which 12 were from rotational photo data and 22 from reflections with high-intensity and high-θ values. Data were collected over the range $4 < 2\theta < 55°$ with $0 < h < 7$, $0 < k < 10$, and $-20 < l < 20$, using the Wyckoff scan technique. Three reflections were checked every 90 measurements, showing no appreciable decay. Data were corrected for Lp effects, and a semiempirical absorption correction was applied. The tungsten atom was located from a Patterson search, the other non-hydrogen atoms were found from subsequent difference Fourier syntheses. Hydrogen atoms were fixed on idealized positions (d_{C-H} = 0.96 Å) and allowed to ride on their carrier atoms. All non-hydrogen atoms were refined anisotropically, and for the hydrogen atoms a common isotropic temperature factor was refined. During the final stages of convergence full-matrix least-squares refinement was applied. Calculations were performed using the SHELX

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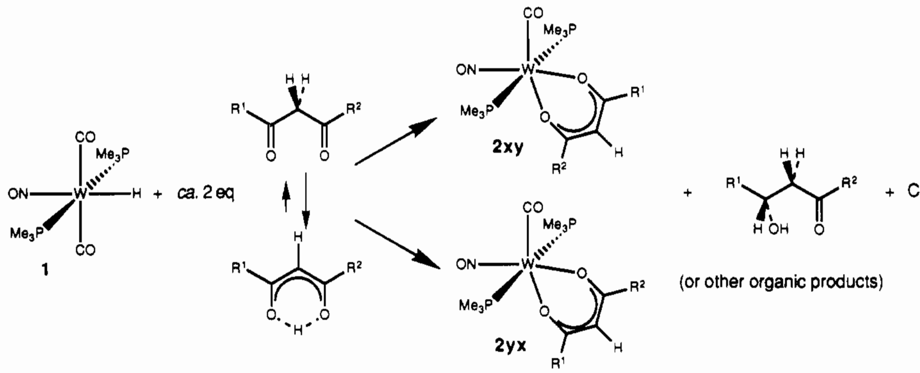
(6) Van der Zeijden, A. A. H.; Sontag, C.; Bosch, H. W.; Shklover, V.; Berke, H.; Nanz, D.; Von Philipsborn, W. *Helv. Chim. Acta* **1991**, *74*, 1194.

Scheme II

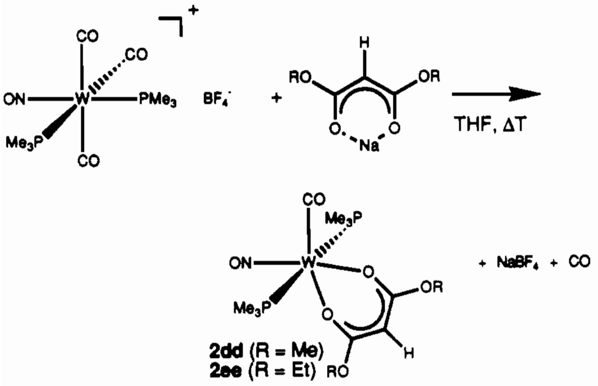


package. Further details of the crystal structure determination are given in Table II. A list of fractional coordinates is given in Table III.

Results and Discussion

Reduction of β-Diketones by 1. The tungsten hydride 1 reacts with a wide variety of β-diketones, according to Scheme II.

The β-diketones used, the reaction conditions, the numbering system of the products **2**, and their yields are given in Table I. The organometallic reaction products were identified (vide infra) as the O,O-chelating tungsten β-diketonates **2**, which could be isolated in good to excellent yields. The four symmetrical β-diketones used ($R^1 = R^2 = CF_3$, Ph, Me, tBu) afforded **2xx** as a single isomer, whereas the six asymmetrical β-diketones used ($R^1 \neq R^2$) afforded a mixture of two isomers **2xy** and **2yx**. It was found that the β-diketone had to contain at least one reducible keto group in order to react, ester groups being not attacked by **1**. From this it follows that diethyl- and dimethylmalonate ($R^1 = R^2$ = OEt, OMe) did not react with **1**. However, the corresponding tungsten β-diketonates **2dd** and **2ee** could also be synthesized by an alternative route not based on **1**; see eq 1.



(1)

From Table I it can be deduced that the influence of the β-substituents R^1 and R^2 on the reaction rate follows the order $CF_3 > Ph \sim Me > OR$, in accord with the decreasing electron-withdrawing properties of these groups. Longer reaction times diminished the overall yield of **2** somewhat, probably due to concurrent decomposition of **1** (which limited the reaction temperature in transformations of **1** to a maximum of ca. 50 °C).

In most cases approximately 2 equiv of β-diketone were needed to drive the reaction to completion. While the course of these reactions was monitored by (low temperature; vide infra) ^1H and ^{13}C NMR, the formation of **2** was found to be accompanied by the liberation of carbon monoxide (^{13}C δ 185 ppm) but also by the formation of reduced organic material, which was characterized by a combination of ^1H and ^{13}C NMR spectroscopy (supplied as supplementary material, Tables S1 and S2). For the three β-keto esters (R^2 = OR, $R^1 = CF_3$, Ph, and Me), formation of **2** was accompanied by equimolar production (^1H NMR integration) of β-hydroxy esters in which the reduction had taken place exclusively on the keto side. Similarly, the reactions of **1** with the four β-diketones containing a CF_3 group ($R^1 = CF_3$, $R^2 = CF_3$, Ph, Me, OEt) afforded equimolar amounts of **2** and the respective β-hydroxy ketones, in which reduction had taken place regiospecifically at the CF_3 side. In analogy, the reaction of **1** with acetylacetone yielded equimolar amounts of **2cc** and 4-hydroxy-2-pentanone. Similar regioselective reductions of β-diketones were reported by use of baker's yeast.[3h,m]

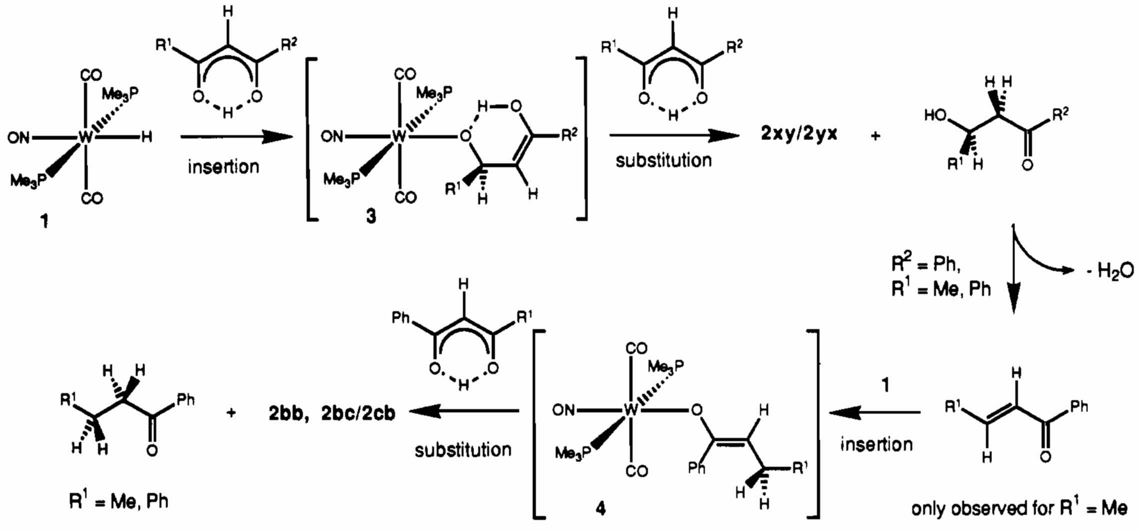
Finally, the remaining two phenyl containing β-diketones led to atypical reduction products. Thus, the reaction of **1** with dibenzoylmethane ($R^1 = R^2$ = Ph) did not produce the expected β-hydroxy ketone, but instead about a *half*-equivalent of its deoxygenated congener 1,3-diphenyl-1-propanone. The reaction of **1** with 1-benzoylacetone (R^1 = Ph, R^2 = Me) produced several organic compounds. In fact, this is the only reduction found, which is not regioselective, since reduction at both the phenyl and the methyl keto side occurs. Thus, reduction of the acetyl group afforded 3-hydroxy-1-phenyl-1-butanone but also its deoxygenated congener, 1-phenyl-1-butanone, while reduction at the phenyl side produced *trans*-4-phenyl-3-buten-2-one, which is the dehydration product of the expected β-hydroxy ketone. The formation of these atypical products may be explained by a mechanism as is depicted in Scheme III.

Thus, an insertion and substitution sequence initially yields a β-hydroxy ketone as the primary reduction product (the presumed intermediate **3** could actually be observed in some cases; vide infra). Normally, the reduction stops at this stage, except when the keto side bears a phenyl residue (R^2 = Ph, R^1 = Ph, Me; not for $R^1 = CF_3$). In that case facile dehydration occurs producing an α,β-unsaturated ketone, which is stabilized by extensive conjugation. Apparently, this ketone is reduced further (fully for R^1 = Ph, partly for R^1 = Me), as long as **1** is still present in solution. We have to assume that an 1,4-addition occurs, affording the intermediate **4** (not observed), which then on substitution produces **2** and a saturated ketone as the final reduction product. We may also conclude that the reduction of the α,β-unsaturated ketone proceeds with a faster (R^1 = Ph) or a competitive (R^1 = Me) rate as compared to that of the original β-diketone.

The presumed intermediacy of the α,β-unsaturated ketone benzalacetophenone (chalcone) during the "double" reduction of dibenzoylmethane to 1,3-diphenyl-1-propanone was made plausible by the following NMR experiment (see Scheme IV). Thus, the reaction of **1** with the commercially available benzalacetophenone in the presence of oxine (which substitutes the β-diketone in its function as an acidic activator and stabilizing ligand for the tungsten moiety), indeed, results in selective formation of 1,3-diphenyl-1-propanone and **5**[1a] after a reaction time of a few hours at room temperature in C_6D_6.

Detection and Characterization of Intermediates 3 by Low-Temperature NMR. The reactions of **1** with the four highly reactive CF_3-containing β-diketones were monitored by NMR, starting at −80 °C in CD_2Cl_2 or toluene-d_8. In all cases the ^1H (Table IV) and ^{13}C (Table V) NMR spectra revealed the formation of intermediates, which were not seen with the other β-diketones (Scheme V). Thus, resonances of the starting

Scheme III



Scheme IV

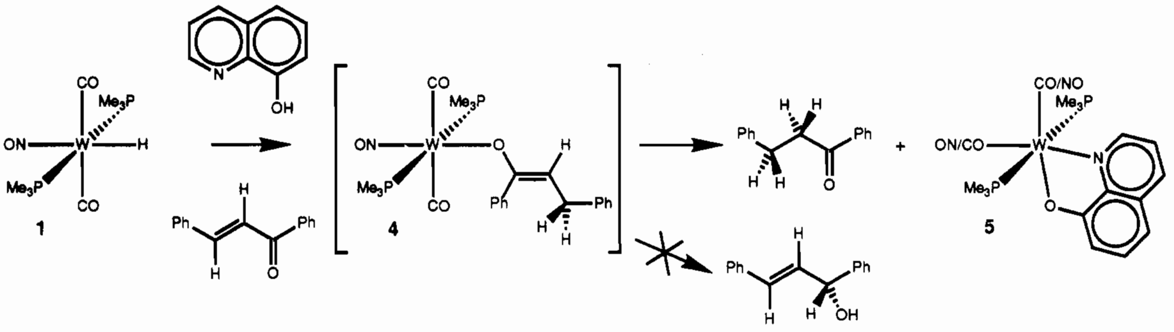
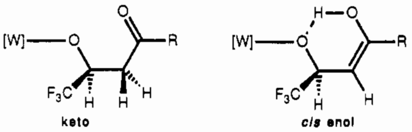


Table IV. ${}^{1}H$ NMR Data (δ) for Intermediates 3[a]

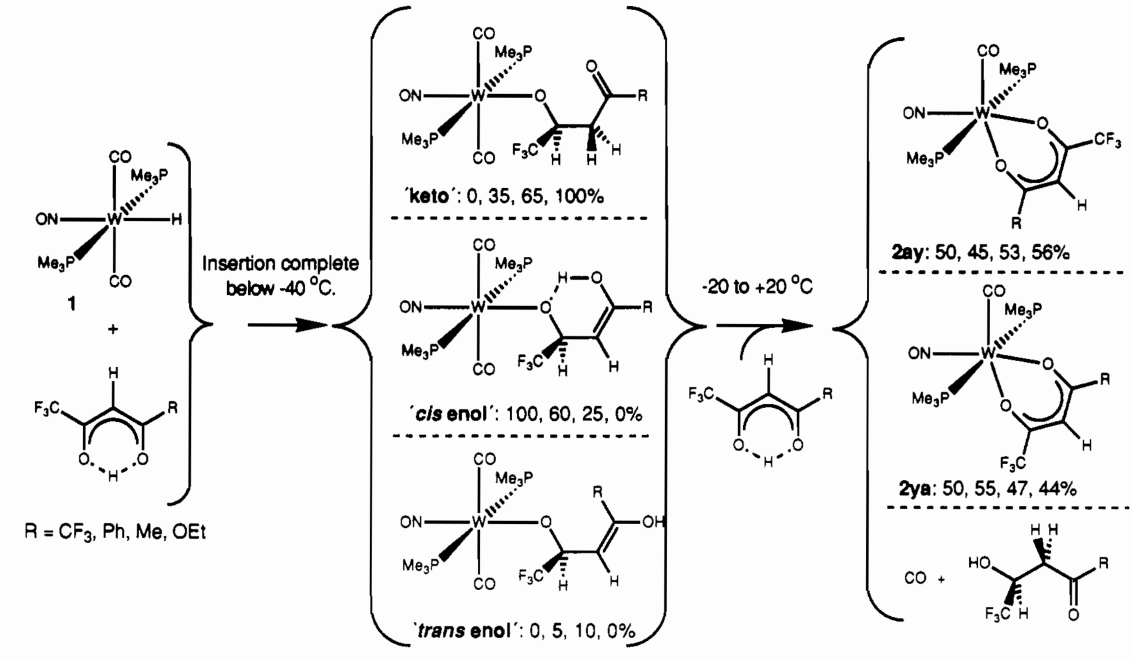


intermediate	solv, temp/°C	R	conformer	rel abund/%	H^1	H^2	OH	R	$P(CH_3)_3$[c]
3aa	toluene-d_8, −50	CF_3	cis enol	100	4.75 (vbr)	6.00 (br)	?		0.96 (?)
3ab	CD_2Cl_2, −40	Ph	cis enol	60	4.41 (qd, 6.6 × 3.5)	4.79 (d, 4.0)	11.59	[d]	1.68 (3.3)
			keto	35	4.20 (m)	2.80 (dd, 3.7 × 14.3)		[d]	1.59 (3.3)
						3.02 (dd, 8.1 × 14.3)			
3ac	CD_2Cl_2, −40	Me	cis enol	25	4.11 (q, br, 7.9)	3.88 (d, br, 3.0)	10.95	[d]	1.66 (d)
			keto	65	3.97 (q, br, 6.3)	2.35 (m)[e]		2.09	1.65 (3.7)
	toluene-d_8, −40		keto	100	4.07 (q, br, 6.6)	2.10 (d, 6.1)		1.65	1.28 (3.7)
3ae	CD_2Cl_2, −40	OEt	keto	100	[d]	2.35 (dd, 3.9 × 14.2)		4.07 (q, 7.3)	1.65 (3.6)
						2.09 (dd, 8.8 × 14.2)		1.20 (t, 7.3)	

[a] [W] = *trans,trans*-$W(CO)_2(NO)(PMe_3)_2$. H^1 is α-positioned relative to the CF_3 group; H^2 is β-positioned. The relative abundancies of the presumed trans enol conformers were too low to allow for a reliable assignment of ${}^{1}H$ signals. [b] Quartet; ${}^{3}J_{CF}$ in parentheses. [c] Triplet; ${}^{2,4}J_{CP}$ in parentheses. [d] Obscured by other resonances. [e] Simulation as an ABC spin system affords $\delta(H^2)$ 2.32, $\delta(H^{2'})$ 2.39 ppm with ${}^{3}J(H^1, H^2)$ = 8.1 Hz, ${}^{3}J(H^1, H^{2'})$ = 4.0 Hz, and ${}^{2}J(H^2, H^{2'})$ = 14.8 Hz.

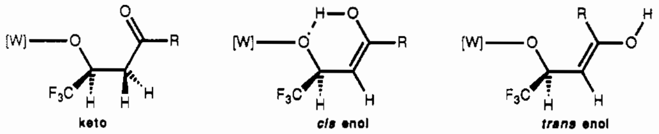
tungsten hydride **1** disappeared between −80 and −40 °C. Instead, the resonances of one (R^2 = CF_3, OEt) or up to three (R^2 = Ph, Me) new tungsten derivatives were observed. They were identified as a mixture of tautomers of tungsten β-ketoalkoxides (**3ay**), which are the result of a selective insertion of the C═O double bond adjacent to the CF_3 group of the β-diketone into the W–H bond of **1**. These compounds were mainly identified by their ${}^{13}C$ NMR spectra (Table V). Thus, the presence of a *trans,trans*-$WX(CO)_2(NO)(PMe_3)_2$ unit is indicated by a single ${}^{13}C$ resonance at ca. 210 ppm with a ${}^{2}J_{CP}$ couplings of ca. 6 Hz that is characteristic of two CO ligands in such an arrangement. The inserted β-diketone must therefore be η^1-bonded to tungsten, most likely through the alkoxy O atom. The ${}^{13}C$ NMR spectra of the keto tautomers clearly reveal the presence of a noncoordinated $–CH_2C(O)R$ unit, with characteristic resonances at 40–45 ppm (CH_2 group) and 170–205 ppm (keto group). The ${}^{1}H$ NMR spectra show the typical multiplet structure of an ABX spin system, with additional quartet ${}^{3}J_{HF}$ coupling on the X nucleus, confirming the presence of the $WOC(CF_3)(H)CH_2R$ unit. The enol forms exhibit characteristic olefinic resonances at ca. 90 and 160 ppm. The phenyl and methyl derivatives, **3ab** and **3ac**, display two such patterns, which we ascribe to the presence of trans and cis enol compounds. The major isomer is probably the one having its OH cis-oriented toward the alkoxy O atom, since in this arrangement extra stabilization can be attained by an intramolecular O–H···O bridge. This was corroborated by the appearance of sharp O–H···O resonances at 11.59 and 10.95 ppm in the ${}^{1}H$ NMR spectra of **3ab** and **3ac**, respectively.

Scheme V. Reaction of **1** with the CF$_3$-Substituted β-Diketones, Started at −80 °C, with Relative Percentages of Reaction Products Given in the Sequence CF$_3$, Ph, Me, and OEt



3ay

Table V. ^{13}C NMR Data (δ) for Intermediates **3**[a]



intermediate	solv, temp/°C	R	confomer	rel abund/%	CF$_3$[b]	C^1 [c]	C^2	C^3	R	W–*C*O[d]	P(*C*H$_3$)$_3$[e]
3aa	toluene-d_8, −50	CF$_3$	cis enol	100	126.9 (300)	69.1 (33)	90.9	147.2[g]	120.2[h]	209.8 (4.4)	16.0 (14.7)
3ab	CD$_2$Cl$_2$, −40	Ph	trans enol	5	*f*	*f*	91.5	157.9	*f*	*f*	*f*
			cis enol	60	126.3 (287)	79.9 (29)	90.7	158.2	*f*	210.6 (6.0)	17.1 (14.3)
			keto	35	*f*	74.4 (27)	42.1	198.8	*f*	209.2 (7.0)	17.3 (14.1)
3ac	CD$_2$Cl$_2$, −50	Me	trans enol	10	126.5 (289)	79[f]	91.0	158.4	20.5	*f*	*f*
			cis enol	25	126.3 (286)	79[f]	90.1	158.9	20.7	210.4	16.9 (14)[f]
			keto	65	127.0 (286)	73.7 (29)	46.6	207.5	32.1	209.5 (6.2)	17.2 (14.2)
	toluene-d_8, −40		keto	100	128.0 (287)	74.1 (28)	46.6	206.0	31.7	210.2 (6.4)	17.1 (14.1)
3ae	CD$_2$Cl$_2$, −40	OEt	keto	100	127.9 (288)	74.2 (29)	39.3	171.5	60.8/13.8	209.5 (6.7)	17.3 (14.5)

[a] [W] = *trans,trans*-W(CO)$_2$(NO)(PMe$_3$)$_2$; the C atoms of the alkoxy backbone C^1, C^2, and C^3 are α, β, γ-positioned relative to the CF$_3$ group. [b] Quartet; $^1J_{CF}$ in parentheses. [c] Quartet; $^2J_{CF}$ in parentheses. [d] Triplet; $^2J_{CP}$ in parentheses. [e] Triplet; $^{2,4}J_{CP}$ in parentheses. [f] Obscured by other resonances. [g] Quartet with $^2J_{CF}$ = 34 Hz. [h] Quartet with $^1J_{CF}$ = 273 Hz.

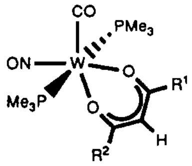
The most striking feature of **3** is its occurrence as a mixture of observable tautomers, which attributes them a unique character in the world of coordination compounds. The question arises whether these tautomers are in (slow) equilibrium. The parent CF$_3$-substituted β-diketone resides almost completely as its cis enol tautomer,[4] and one would therefore expect only the cis enol tautomer of **3** as the kinetic insertion product. The fact that this is not the case suggests that the various tautomers of **3** are in thermodynamic equilibrium. This is corroborated by the observation that the influence of the β-substituent R^2 on the keto/enol ratio parallells that of the electron-withdrawing capability of R^2. Thus, for the series OEt, Me, Ph, and CF$_3$ in CD$_2$Cl$_2$ we observe a dramatic increase of the enol forms from 0 to 35, 65, and 100%, respectively. The keto/enol ratio is also dependent on the type of solvent. Whereas this ratio for **3ac** is 65:35 in the more polar solvent CD$_2$Cl$_2$, it reaches a 100:0 ratio in the more apolar medium toluene-d_8, a behavior which actually contrasts that of the keto/enol equilibrium of the parent β-diketones.[4a]

When the temperatures of solutions of **3** were further raised to about −20 to +20 °C, a second equivalent of β-diketone substitutes the alkoxy moiety in **3**, affording the two isomers **2ay** and **2ya**, the β-hydroxy ketone HOC(CF$_3$)(H)CH$_2$C(O)R, and free carbon monoxide. For **3ab** and **3ac** it was noticed that the keto and trans-enol tautomer disappeared somewhat faster from the reaction mixture than the cis-enol tautomer. This may be due to the fact that the O$_{\text{alkoxy}}$ atom in the former tautomers is somewhat more susceptible for substitution by a β-diketone than the analogous O atom of the cis-enol tautomer, which is presumed to be involved in intramolecular H bonding. However, it is also possible that the keto–enol equilibrium simply shifts to the enol side at higher temperatures.

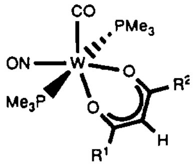
Although compounds **3** have the geometrical disposition to form an O,O′-chelate complex, via extrusion of a CO ligand and coordination of the keto moiety, they apparently do not. This is contrasted by the fact that the substitution of the β-keto alkoxy moiety in **3** by a β-diketone does afford an O,O′-chelate complex. This difference may be explained by the extra stabilization that is gained in the latter case through the quasi aromatic character of the chelate ring in **2**, which could not be attained when the alkoxy moiety in **3** would cyclize.

Isomeric Mixtures 2xy and 2yx in Solution. The reaction of **1** with those β-diketones that have different β-substituents (R^1 ≠ R^2, 6 entries) produces a mixture of two isomers (Table VI), which only differ in the relative positions of the CO and NO

Table VI. Isomer Ratios for the Asymmetrical Tungsten β-Diketonates



2xy



2yx

no.	R^1	R^2	reacn time, temp/°C, solv	2xy:2yx	after storage for $^1/_2$ year as a solid[d]	after equilibration with PMe_3 in C_6D_6
2ab/2ba	CF_3	Ph	1 h, 50, toluene	57:43[a]	58:42 (57:43)	62:38
			−80 to 20, in CD_2Cl_2	45:55		
2ac/2ca	CF_3	Me	$^1/_2$ h, 20, toluene	71:29[a]	100:0 (100:0)	59:41
					78:22 (0:100)	59:41
			−80 to 20, toluene-d_8	48:52		
			−80 to 20, in CD_2Cl_2	53:47		
			10 min, 70, C_6D_6	58:42		
			$^1/_2$ h, 20, CD_3OD	56:44[c]		
			1 h, reflux, THF[b]	60:40[a]		
2ae/2ea	CF_3	OEt	3 h, 20, toluene	60:40[a]	87:13 (60:40)	63:37
			−80 to 20, CD_2Cl_2	56:44		
			15 min, 70, C_6D_6	55:45		
			1 h, 20, CD_3OD	59:41[c]		
2bc/2cb	Ph	Me	3 d, 50, toluene	55:45[a]	100:0 (100:0)	52:48
					0:100 (0:100)	52:48
2be/2eb	Ph	OEt	8 d, 50, toluene	66:34[a]	70:30 (66:34)	61:39
2cd/2dc	Me	OMe	6 d, 50, toluene	61:39[a]	55:45 (61:39)	62:38

[a] Isolated product. [b] Synthesized by the reaction of [*cis,mer*-$W(CO)_3(NO)(PMe_3)_2$][BF_4] with Li(β-diketonate). [c] This reaction results in deuteration of the α-H atom in **2xy**/**2yx**. [d] Starting values are given between parentheses; note that the isomer mixtures **2ac**/**2ca** and **2bc**/**2cb** were separated by chromatography.

Table VII. ^1H, ^{31}P, and ^{19}F NMR Data (δ) for **2**[a]

no.	R^1	R^2	$^1H/^{19}F$ NMR				^{31}P NMR
			R^1	>C*H*	R^2	$P(CH_3)_3$[b]	*P*Me_3[c]
2aa	CF_3	CF_3	*-75.64*	6.30	*-75.25*	0.89 (3.5)	-8.95 (305)
2ab	CF_3	Ph	*-74.97*	6.58	7.0 (m), 7.7 (m)	0.99 (3.4)	-9.03 (307)
2ba	Ph	CF_3	7.0 (m), 7.7 (m)	6.60	*-74.62*	0.97 (3.4)	-9.25 (307)
2ac	CF_3	Me	*-75.29*	5.59	1.66	0.98 (3.7)	-9.30 (311)
2ca	Me	CF_3	1.46	5.61	*-74.94*	0.98 (3.7)	-9.04 (308)
2ae	CF_3	OEt	*-75.56*	5.39	0.94, 3.84	1.07 (3.5)	-8.78 (308)
2ea	OEt	CF_3	0.85, 3.65	5.41	*-75.12*	1.05 (3.5)	-9.20 (309)
2bb	Ph	Ph	7.2 (m), 7.9 (m)	6.88	7.2 (m), 7.9 (m)	1.06 (3.2)	-9.10 (309)
2bc	Ph	Me	7.1 (m), 7.8 (m)	5.99	2.00	1.05 (3.0)	-8.78 (309)
2cb	Me	Ph	1.78	5.99	7.1 (m), 7.8 (m)	1.06 (3.3)	-8.73 (309)
2be	Ph	OEt	7.1 (m), 7.7 (m)	5.78	1.06, 4.00	1.11 (3.3)	-8.41 (310)
2eb	OEt	Ph	0.97, 3.81	5.77	7.1 (m), 7.9 (m)	1.10 (3.3)	-8.54 (310)
2cc	Me	Me	1.58	5.07	1.81	1.07 (3.4)	-8.92 (311)
2cd	Me	OMe	1.59	4.90	3.36	1.11 (3.4)	-8.59 (311)
2dc	OMe	Me	3.17	4.91	1.84	1.09 (3.4)	-8.59 (311)
2dd	OMe	OMe	3.18	4.70	3.39	1.11 (3.5)	-8.31 (311)
2ee	OEt	OEt	0.92, 3.74	4.72	1.02, 3.96	1.16 (3.4)	-8.46 (304)
2ff	tBu	tBu	1.00	5.68	1.11	1.12 (3.4)	-10.77 (309)

[a] In C_6D_6 at +22 °C; ^1H, ^{31}P, and ^{19}F data are given in ppm relative to C_6D_5H (7.15 ppm), external H_3PO_4, and external $CFCl_3$, respectively; ^{19}F chemical shifts are given in italic figures. Ethyl groups have triplet and quartet resonances, respectively, with $^3J(H,H)$ = 7.1 Hz. [b] $^{2,4}J(H,P)$ between parentheses. [c] $^1J(P,^{183}W)$ between parentheses.

ligands. Due to the very similar spectroscopic data (^1H, ^{19}F, and ^{31}P NMR, Table VII; ^{13}C NMR, Table VIII; IR, Table IX; UV/vis, Table X), it appeared rather difficult to distinguish the two isomers (see the next paragraph for a discussion on this matter). From the, at first sight rather confusing, data in Table VI it can firstly be seen that the isomeric ratios roughly vary from 1:1 to 2:1. There is a slight preference for the isomer **2xy**, in which the more electron-withdrawing group is quasi trans to the NO ligand. This is in accord with thermodynamic considerations: a kind of push–pull effect induces the strongest π-acceptor (NO) to be positioned trans to the strongest π-donor, being the O atom of the β-diketonate with the more electron-withdrawing group in its neighborhood, giving this side more enolate character and hence more π-electron density on the O atom.[7]

In rationalizing the observed isomeric ratios, it is important to find out whether we deal with a kinetically or thermodynamically dominated situation. If the latter is true, we have to assume an exchange reaction between the isomers **2xy** and **2yx**. Actually, we discovered that an exchange process does take place, but it is extremely slow. It is slow enough to allow separation of the isomers by column chromatography, which was accomplished with **2ac**/**2ca** and **2bc**/**2cb**. We also discovered that the exchange between **2xy** and **2yx** may be accelerated considerably in the presence of PMe_3 (this shortens this equilibration process from a few months to a few hours at room temperature). A similar PMe_3-catalyzed isomerization was recently reported by us (Scheme VI).[8] We think the mechanism involves the prior coordination of PMe_3 to the tungsten center with simultaneous bending of the NO ligand in order to keep up with the 18-electron

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(7) Holl, M. M.; Hillhouse, G. L.; Folting, K.; Huffman, J. C. *Organometallics* **1987**, *6*, 1522.

(8) Van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 563.

Table VIII. ^{13}C NMR Data for **2**[a]

			δ						
no.	R^1	R^2	R^1	C^1	C^2	C^3	R^2	$P(CH_3)_3$	W–CO
2aa	CF_3	CF_3	118.7 [284]	171.1 [35]	93.4	171.6 [35]	118.2 [283]	13.4 (13.5)	238.7 (3.5)
2ab	CF_3	Ph	119.8 [283]	168.4 [33]	93.67	185.1	137.3, 129.1, 127.1, 132.2	14.0 (12.8)	242.3 (3.6)
2ba	Ph	CF_3	137.3, 129.0, 127.1, 132.4	184.9	93.3	169.5 [33]	119.3 [283]	14.0 (12.8)	243.7 (3.6)
2ac	CF_3	Me	119.4 [284]	167.7 [33]	97.4	194.3	27.9	14.0 (13.0)	243.0 (3.5)
2ca	Me	CF_3	27.3	194.4	96.8	168.8 [33]	118.9 [284]	14.0 (13.0)	244.0 (3.4)
2ae	CF_3	OEt	119.7 [282]	170.2 [33]	85.3	171.5	14.0, 61.5	14.1 (13)	244.1 (3.7)
2ea	OEt	CF_3	14.0, 61.3	173.7	82.8	170.8 [33]	119.4 [283]	14.1 (13)	246.6 (3.6)
2bb	Ph	Ph	139.3, 128.8, 127.0, 131.2	181.1	94.5	182.4	139.3, 128.7, 127.1, 131.1	14.3 (12.0)	246.0 (3.5)
2bc	Ph	Me	138.6, 128.7, 127.0, 131.2	180.1	97.7	189.8	27.9	14.4 (12.6)	246.3 (3.7)
2cb	Me	Ph	27.2	188.8	97.9	181.4	138.6, 128.7, 127.2, 131.1	14.4 (12.6)	246.7 (3.9)
2be	Ph	OEt	139.0, 128, 126.7, 130.7	181.9	83.5	172.0	14.4, 60.3	14.4 (12.0)	246.6 (3.6)
2eb	OEt	Ph	14.4, 60.1	173.6	81.5	182.8	139.3, 128, 126.9, 130.6	14.4 (12.0)	248.5 (3.6)
2cc	Me	Me	26.4	187.6	101.3	188.7	27.0	14.4 (11.6)	246.6 (3.4)
2cd	Me	OMe	26.4	188.5	85.7	171.3	51.0	14.3 (12.6)	246.4 (4.0)
2dc	OMe	Me	50.6	172.8	83.9	189.2	27.0	14.3 (12.6)	248.5 (4.0)
2dd	OMe	OMe	50.6	175.8	66.5	174.4	50.8	14.2 (12.7)	247.7 (3.6)
2ee	OEt	OEt	14.4, 59.6	175.7	67.0	174.3	14.4, 59.7	14.4 (12.2)	247.9 (3.6)
2ff	tBu	tBu	28.5, 40.8	197.0	91.7	198.1	28.5, 41.7	15.0 (12.3)	245.9 (3.4)

[a] Measured in C_6D_6 (128.0 ppm) at +22 °C. $J(^{13}C-^{19}F)$ (q) in brackets. $J(^{13}C-^{31}P)$ (t) in parentheses.

Table IX. IR Absorptions in the 1500–2200-cm^{-1} Region for **2**[a]

no.	R^1	R^2	ν(CO)	ν(NO)	phenyl	ester
2aa	CF_3	CF_3	1917	1622		
2ab/2ba[b]	CF_3/Ph		1902	1610	1556	
2ac	CF_3	Me	1903.7	1610.8		
2ca	Me	CF_3	1900.6	1612.8		
2ae/2ea[b]	CF_3/OEt		1897	1610		1632
2bb	Ph	Ph	1891	1598	1516	
2bc	Ph	Me	1890.8	1600.4	n.o.[c]	
2cb	Me	Ph	1892.5	1599.5	n.o.	
2be/2eb[b]	Ph/OEt		1889	1598	1511	n.o.
2cc	Me	Me	1891	1600		
2cd/2dc[b]	Me/OMe		1890	1598		1611 (sh)[d]
2dd	OMe	OMe	1889	1603		1623
2ee	OEt	OEt	1889	1602		1620
2ff	tBu	tBu	1891	1598		

[a] In cm^{-1}; IR spectra were measured in hexane. ν(CO) has strong intensity, ν(NO) has medium to strong intensity, and others are weak. [b] Measured as a mixture of isomers. [c] n.o. = not observed. [d] sh = shoulder.

count (Scheme VI). The resulting seven-coordinated tungsten(II) intermediate should then be subject to a facile ligand scramble.

Furthermore, it was found that the addition of PMe_3 to a solution of a certain isomeric mixture **2xy**/**2yx** obtained under different conditions and with different isomeric ratios always converges to the same value, which we assume therefore be representative of thermodynamic conditions (last column in Table VI). Even the separated isomers **2ac** and **2ca**, as well as **2bc** and **2cb**, equilibrated rapidly to the same isomeric ratios after addition of PMe_3 (to 59:41 and 52:48, respectively).

When the thermodynamical isomeric ratios are compared with the other values in Table VI, it can be seen that the reactions of **1** with the three asymmetrically, CF_3-substituted β-diketones, which were started at −80 °C, produced a larger amount of the less stable isomer **2yx**. Obviously, there is a kinetic preference for this isomer during the substitution of the alkoxy moiety in intermediate **3** by a β-diketone (see Scheme IV). Since however the intimate details of this substitution are not known (for instance concerning the question at which stage loss of CO occurs), it is difficult to rationalize this observation.

The thermodynamically determined isomeric ratios allow us to calculate the energy differences between **2xy** and **2yx**. These values do not exceed 1.3 kJ/mol (between **2ae** and **2ea**). It can also be concluded that the electronic influence of the Me and Ph groups on the relative stability is virtually identical.

Isomeric Mixtures 2xy and 2yx in the Solid State. After being stored as a *solid* for 1/2 year at room temperature under nitrogen and normal laboratory light, all six isomeric mixtures **2xy**/**2yx** were remeasured by ^1H NMR in C_6D_6. Whereas the clear solutions did not show any appreciable decomposition, in several cases we noticed a dramatic change in the isomeric ratios (especially those of **2ac**/**2ca** and **2ae**/**2ea**; see second to last column of Table VI). In three cases (**2ac**/**2ca**, **2ae**/**2ea**, and **2be**/**2eb**) a shift toward the more stable isomer **2xy** was observed and in one case (**2cd**/**2dc**) a shift toward the less stable isomer **2yx** was seen, while in two cases (**2ab**/**2ba** and the separated isomer pair **2bc** and **2cb**) no significant change was found. Apparently, conversions from one isomer into the other have taken place in the *solid* state. Addition of an excess of PMe_3 to the NMR tube resulted in the reestablishment of the thermodynamic isomeric ratios (last column in Table VI) within a few hours.

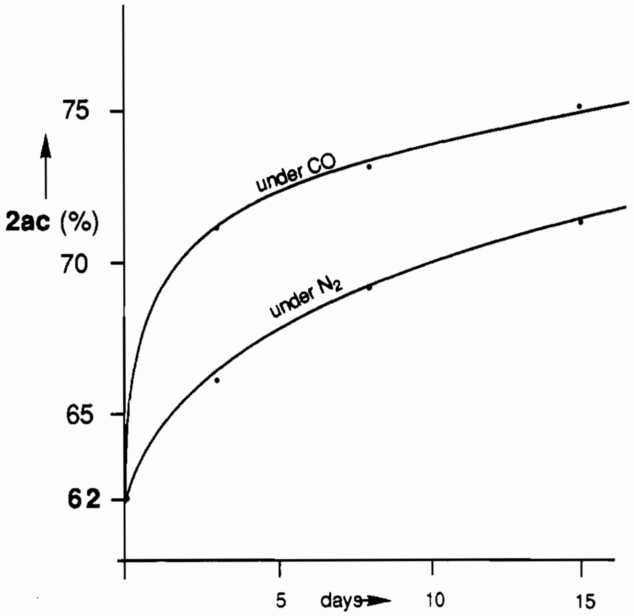


Figure 1. Conversion of **2ca** into **2ac** in the solid state at 55 °C, monitored by ^1H NMR in C_6D_6.

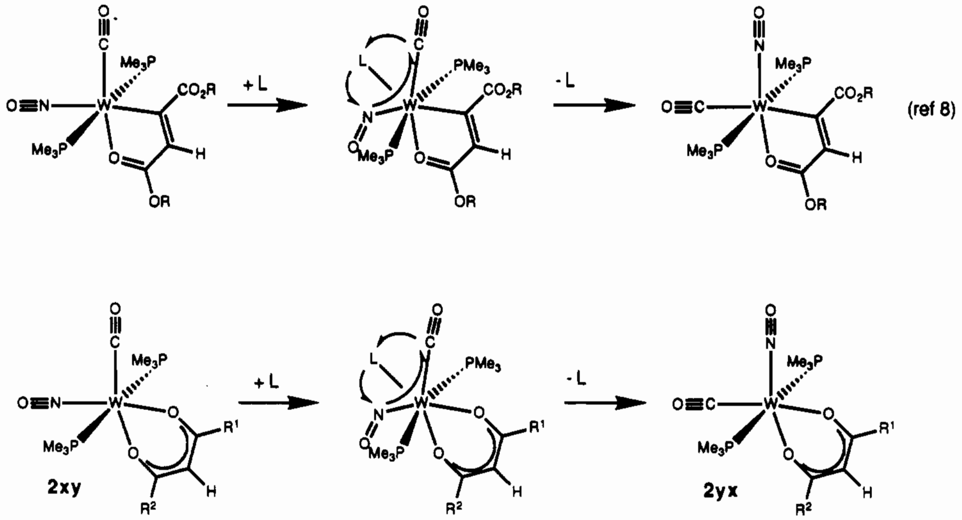
The solid-state phenomena of **2ac**/**2ca** were studied in greater detail. Thus, it was found that the separated, more stable isomer **2ac** was not converted to **2ca**, even on prolonged storage at 100 °C. On the other hand, solid **2ca** readily rearranges to **2ac** over a period of months at room temperature (78% in 6 months). In a further experiment, a batch of **2ac** and **2ca**, obtained as a 62:38 mixture, was divided over two Schlenk tubes; one was put under an atmosphere of nitrogen and the other under carbon monoxide and both stored at 55 °C, while samples were taken regularly and analyzed by ^1H NMR in C_6D_6 (Figure 1). It was found that in both tubes conversions from **2ca** to **2ac** took place, but from

Table X UV/Vis Data for **2**[a]

no.	R¹	R²	color	π–π* transitions	d–d	MLCT1	MLCT2	other
1			orange		345 (2300)			445 (100)
2aa	CF_3	CF_3	purple	*245 (8800)*, *265 (7400)*	318 (2600)	492 (2000)	520 (2000)/640 (2000)	
2ab/**2ba**[b]	CF_3/Ph		black	274 (13 000), 319 (9000)	obscured	466 (2700)	600 (2700)	
2ac	CF_3	Me	red-purple	280 (5900)	342 (2100)	424 (2100)	530 (1700)	
2ca	Me	CF_3	red-purple	280 (5900)	344 (2200)	426 (1900)	539 (2000)	
2ae/**2ea**[b]	CF_3/OEt		red	*275 (6000)*	327 (3800)	*370 (1500)*	*450 (1000)*	
2bb	Ph	Ph	(hexane)	248 (27 000), 278 (15 000), 339 (17 000)	obscured	471 (3200)	604 (2800)	
			black	234 (15 000), 277 (14 000), 339 (17 000)	obscured	441 (3800)	575 (2900)	
			(DMSO)	*276 (14 000)*, 337 (16 000)	obscured	446 (3800)	573 (2900)	
2bc	Ph	Me	red-purple	246 (15 000), 260 (16 000), 309 (13 000)	*348 (4000)*	419 (2200)	515 (1800)	
2cb	Me	Ph	red-purple	239 (15 000), 259 (14 000), 312 (12 000)	359 (3500)	409 (3400)	514 (2600)	
2be/**2eb**[b]	Ph/OEt		brown	245 (10 000), 284 (14 000)	*337 (1500)*		*418 (1100)*	
2cc	Me	Me	(hexane)	283 (11 000)	339 (3500)	389 (2000)	456 (1400)	
			orange	279 (12 000)	334 (3600)	*380 (2000)*	444 (1600)	
			(DMSO)	278 (12 000)	336 (3600)	*377 (1500)*	437 (1500)	
2cd/**2dc**[b]	Me/OMe		orange	*247 (8000)*, *268 (4000)*	335 (1300)		392 (1000)	
2dd	OMe	OMe	orange	247 (6500)	342 (1000)	270 (5100)	342 (1000)	407 (700)
2ee	OEt	OEt	orange	244 (5000)	337 (1000)	273 (4000)	337 (1000)	385 (800)
2ff	tBu	tBu	orange	282 (10 000)	333 (3500)	*374 (1800)*	439 (1600)	

[a] In nm (ε in L cm^{-1} mol^{-1} in parentheses). UV/vis spectra were measured in dichloromethane unless stated otherwise; values in italics were poorly resolved. [b] Measured as a mixture of isomers.

Scheme VI [a]



[a] L = CO and PMe_3.

Figure 1 it is clearly seen that the conversion proceeds much faster in the presence of gaseous CO. Decomposition was not observed thereby, since the samples dissolved completely in C_6D_6, and no compounds other than **2ac** and **2ca** were seen. The conversions do not go to completion (100:0 ratio), but both seem to approach a value that is close to the 78:22 ratio obtained after the solid-state conversion of pure **2ca**.

Some conclusions can be drawn from the above observations. First, in the solid state an isomeric ratio **2xy**:**2yx** is strived for which differs from that in solution. In solution the **2xy**/**2yx** ratio is governed by different electronic forces within the molecule and solvation effects, whereas in the solid state it is determined by electrostatic forces between molecules in the crystal lattice. These electrostatic forces determine the molecular packing, and differences thereof between those of **2xy** and **2yx** will probably determine which of two is being prefered in the solid state, a preference that might even contradict that in solution like for **2cd**/**2dc**.

The conversions are obviously catalyzed by CO, and we think a mechanism is operative similar to that of the PMe_3-catalyzed isomerization in solution (see Scheme VI). Although a crystal lattice restricts the mobility of molecules considerably, we have to assume that free CO is capable of penetrating some of the crystal lattices and inducing the isomerization. However, these isomerizations also occur in the absence of gaseous CO, and we assume therefore that coordinated CO is reversibly released from some molecules in the crystal and induces the isomerization of neighboring molecules. Some isomer pairs do (almost) not interconvert, like **2ab**/**2ba**, **2bc**/**2cb**, and **2be**/**2eb**, which might be due to the impossibility of CO to penetrate the crystal lattice in these cases. In this sense, our observations may be compared with those of Arjulan et al., who studied the oxidation of thioketones by molecular oxygen in solution and in the crystal.[9] It was found that certain thioketones which were readily oxidized in solution were stable in the solid state, which was attributed to a specific molecular packing that did not allow oxygen molecules to diffuse into the crystal. In this respect, it is interesting to look at Figure 4 (see further section for a detailed discussion on the X-ray molecular structure of **2ac**), which shows the molecular packing of **2ac** down to *c* axis and reveals possible channels along which CO molecules might penetrate the crystal.

Identification and Properties of 2. The present series of 12 compounds (18 if all isomers are included) presents a unique type of neutral, zerovalent tungsten β-diketonates and may be compared with the isoelectronic d⁶ complexes $[Et_4N][W(CO)_4(\beta\text{-diketonate})]$[10] and $Re(CO)_4(\beta\text{-diketonate})$[11] or with the d⁸

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(9) (a) Arjulan, P.; Ramamurthy, V.; Venkatesan, K. *Acta Crystallogr.* **1984**, *C40*, 552. (b) *Ibid.*, p 556. (c) See also: Shklover, V. E.; Timofeeva, T. V. *Uspekhi Khim.* **1985**, *54*, 1057 (p 619 of *Russ. Chem. Rev.*). Shklover, V. E.; Timofeeva, T. V.; Struchkov, Yu. T. *Uspekhi Khim.* **1986**, *55*, 1282 (p 721 of *Russ. Chem. Rev.*).

(10) Doyle, G. *J. Organomet. Chem.* **1973**, *61*, 235.

complexes $M(CO)_2$(β-diketonate) with M = Rh[12] and Ir.[13] They are all air stable, although the ester-containing ones decompose over a period of months in air. The compounds have various colors, ranging from orange to red, purple, and even black; vide infra. The presence of a number of NMR-active nuclei (^1H, ^{13}C, ^{19}F, ^{31}P, and ^{183}W) as well as IR-active moieties (CO, NO) in **2** offers an unique opportunity for a detailed study of these complexes, especially with respect to the electronic influences of the two β-substituents and the CO and NO ligands.

(a) IR Spectra. The IR data for **2** are listed in Table IX. The IR data for the separated isomeric pairs **2ac**/**2ca** and **2bc**/**2cb** show very little difference. This suggests that the electronic influence of a β-substituent gets more or less delocalized over the six-membered chelate ring and is spread equally well over the CO and NO ligands and does therefore certainly not give rise to an exclusive trans influence. Introduction of the powerful electron-withdrawing CF_3 group on the β-diketonate enhances its π-acceptor capability, which is demonstrated by the higher ν(CO) and ν(NO) stretching frequencies as a result of a weaker bond between the respective ligands and tungsten. Except for the CF_3 substituent, the electronic effects of the other substituents on the CO and NO ligands are strikingly similar. There is a linear correlation between ν(CO) and the ^{13}C chemical shift of the CO group (δ(CO))

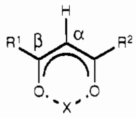
$$\delta(\mathrm{CO}) = 835.2 - 0.311[\nu(\mathrm{CO})] \quad (r = 0.985 \text{ for } n = 12)$$

a correlation which has been observed in a number of other complexes too.[14]

(b) NMR Spectra. The ^1H, ^{19}F, and ^{31}P NMR data of **2** are listed in Table VII; the ^{13}C NMR data in Table VIII. From the very similar ^1H, ^{13}C, and ^{31}P resonances of the PMe_3 ligands it can be concluded that electronic influences of the β-substituents are almost exclusively exerted in the plane of the β-diketonate ligand. In the case of the isomeric mixtures the NMR spectra were measured as such. Separation of the data into two sets of resonances was usually easily accomplished on the basis of intensity differences. Only for the pair **2bc**/**2cb**, which exist almost as a 50:50 mixture, was this not possible; therefore, these isomers were separated by column chromatography and measured separately.

As mentioned before, a major problem represented the discrimination of the isomers **2xy** and **2yx**. First, the NMR signals were divided into two groups, by looking for analogies among these data. In order to have any success with this strategy, derivatives of **2** had to be synthesized with as many as possible combinations of CF_3, Ph, Me, and O_{alkyl} groups. Thus, it was found that the NMR resonances of a certain β-substituent **x** of two related isomer pairs **2xy** and **2yx** show a chemical shift difference that was almost identical to that of another isomer pair **2xz** and **2zx**, containing the same β-substituent **x**. For instance, the ^{19}F and ^{13}C NMR data of the seven CF_3-containing complexes reveal a remarkably constant difference of +0.38 (±0.02) and +0.42 (±0.13) ppm, respectively, between those of isomer **2ax** and **2xa** (or in **2aa**). Similarly, the ^1H and ^{13}C resonances of the seven methyl-containing complexes show a very constant difference of +0.23 (±0.02) and +0.62 (±0.01) ppm between those of **2cx** and **2xc**. Also, the ^1H resonances of the ester groups in **2dx** or **2ex** can be found at consistently higher field as those of **2xd** or **2xe**. Only the ^1H and ^{13}C resonances of the phenyl groups are too similar to draw any meaningful conclusions therefrom. Finally, it was found that the ^{13}C resonances of the β carbons of the β-diketonates (C1 and C3 in Table VIII) also show systematic trends. In addition, it is to be noted that through these analogies it also proved possible to assign the resonances of the symmetrical β-diketonates **2xx** with great reliability. By these analogies it was thus possible to divide the resonances of all 18 compounds up into two sets. The final problem was to relate the two groups to either **2xy** or **2yx** by some reference. This was accomplished by the determination of an X-ray structure of one representative member of the series, namely **2ac**, which turned out to have the CF_3 group in a quasi trans position to the NO group (see section e for further details on this structure).

Table XI. ^1H and ^{13}C NMR Increments[a]



$\delta(C_\alpha) = K_\alpha + \Delta(R^1)_\alpha + \Delta(R^2)_\alpha$ $\delta(C_\beta) = K_\beta + \Delta(R^1)_n + \Delta(R^2)_d$ $\delta(H) = K_H + \Delta(R^1)_H + \Delta(R^2)_H$

X	H				$W(CO)(NO)(PMe_3)_2$[b]				$W(CO)_4^-$	$Ir(CO)_2$	$Rh(CO)_2$
Source	Ref 14a				This Work				Ref 9	Ref 12	Ref 11
Solvent	^{13}C: CCl_4, ^1H: $CDCl_3$				C_6D_6 ($CDCl_3$)[e]				CD_3CN	$CDCl_3$	CCl_4
K_α, K_β, K_H	100.6	191.5		*5.49*	100.8	188.5		*5.06(5.38)*	*5.33*	*5.74*	*5.52*
R^1/R^2	$\Delta(R)_\alpha$	$\Delta(R)_n$	$\Delta(R)_d$	$\Delta(R)_H$[c]	$\Delta(R)_\alpha$	$\Delta(R)_n$	$\Delta(R)_d$	$\Delta(R)_H$	$\Delta(R)_H$	$\Delta(R)_H$	$\Delta(R)_H$
CF_3	-4.1	-14.9	3.5	*0.44*	-3.2	-20.5	3.6	*0.59 (0.46)*	*0.36*	*0.46*	*0.49*
Ph	-4.2	-8.5	2.0	*0.66*	-3.2	-7.7	1.0	*0.91(0.73)*	*0.71*	*0.66*	*0.66*
tBu	-5.1	8.8	0.4	*0.12*	-4.6	d	d	*0.31*	*0.18*		
OR	-	-	-	-	-15.8	-17.0	2.0	*-0.19 (-0.21)*	*-0.61*		

[a] All increments for R^1/R^2 = Me were fixed at 0. Values referring to ^1H NMR data are given in italics. [b] Data for isomers **2xy** and **2yx** were averaged. [c] Data from: Bassetti, M.; Cerichelli, G.; Floris, B. *Gazz. Chim. Ital.* **1986**, *116*, 579. [d] $\Delta(tBu)_n + \Delta(tBu)_d = +9.1$. [e] Data in $CDCl_3$ are unpublished results.

The wealth of NMR data available for **2** offers the opportunity to study systematic substituent effects. Russian scientists found that for the enol form of β-diketones as well as for their BF_2 derivatives the ^{13}C resonances of the α- and β-carbons may be calculated for by a simple summation of group-specific increments (Table XI).[15] The calculated increments and constants were found to be rather insensitive to the replacement of the proton by the BF_2 group. Except for the CF_3 group, we also observed little difference between our calculated values and those of the parent β-diketones (Table XI).[16] The ^1H chemical shift of H_α may be described by a similar formula. Comparison of the resulting increments for different systems reveals a striking uniformity, whereas some dispersion is observed for the reference constant K_H. Changing to an anisotropical solvent like C_6D_6 results in some deviations.

The ^{13}C chemical shifts of the CO ligands in **2** (δ(CO)) could only be moderately fitted to a similar linear relationship (r = 0.975; the resonances of isomers **2xy** and **2yx** were averaged). However, a surprisingly good *multiplicative* relationship was found (r = 0.997):

$$\delta(\mathrm{CO}) = 250.8 - \Delta(R^1)(\Delta(R^2))$$

$$\Delta(R) = 3.45\ (\mathrm{CF_3}),\ 2.15\ (\mathrm{Ph}),\ 2.05\ (\mathrm{Me}),\ \text{and}\ 1.65\ (\mathrm{OR})$$

Although it is difficult to judge the physical significance of this formula, we notice that the calculated factors Δ(R) show a very good linear relationship with Hammett's parameter σ_p (r = 0.99)[13,17] but not with σ_m (r = 0.84). This suggests that the

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(15) (a) Shapet'ko, N. N.; Berestova, S. S.; Lukovkin, G. M.; Bogachev, Y. S. *Org. Magn. Reson.* **1975**, *7*, 237. (b) Shapet'ko, N. N.; Berestova, S. S.; Medvedeva, V. G.; Skoldinov, A. P.; Andreichikov, Y. S. *Dokl. Acad. Nauk USSR* **1977**, *234*, 566. (c) Berestova, S. S.; Shapet'ko, N. N.; Shigorin, D. N.; Medvedeva, V. G.; Skoldinov, A. P.; Plakhina, G. D.; Andreichikov, Y. S. *Theoret. Exp. Chem.* **1979**, *15*, 449. See also ref 4a and: Bassetti, M.; Cerichelli, G.; Floris, B. *J. Chem. Res.* (*S*) **1988**, 236.

(16) These data allow us to estimate the NMR data for the hypothetical enolate form of dialkylmalonate: $\delta(C_\alpha) \approx 68$, $\delta(C_\beta) \approx 173$, and $\delta(H_\alpha) \approx 4.65$ ppm.

(17) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

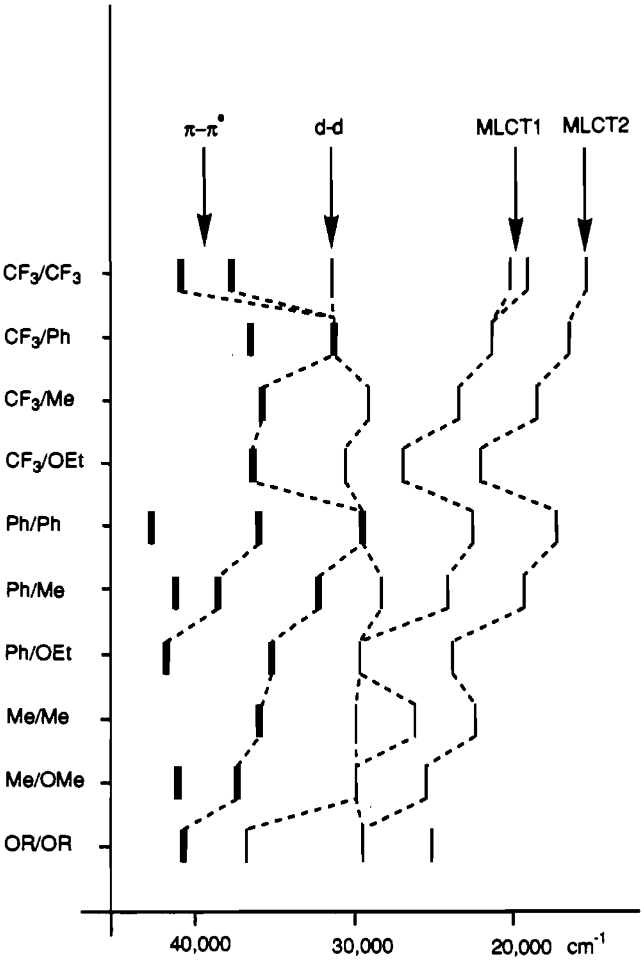

Figure 2. Electronic spectra of **2**. Compound **2ff** is omitted. Values for **2dd** and **2ee** were averaged. Related transitions are connected by dashed lines.

electronic effects of β-substituents on NMR and IR parameters mutually reinforce each other.

(c) UV/Vis Spectra. The electronic spectra of **2**, measured in the 200–800-nm region (12 500–50 000 cm^{-1}), also show some interesting analogies (see Table X and Figure 2). As for the other spectroscopic parameters, the separated asymmetrical tungsten β-diketonates **2ac**/**2ca** and **2bc**/**2cb** display only very little difference. All complexes exhibit two absorptions (called MLCT1 and MLCT2) in the visible region, with a rather constant separation (5200 ± 1200 cm^{-1}). For compounds **2bb** and **2cc** these bands shift hypsochromically on going to a more polar solvent, which is typical of a metal to ligand charge-transfer (MLCT) transition.[18] We assign these two bands to transitions from a quasi "t_{2g}" electron reservoir to one of the two π^* levels of the β-diketonate.[19] Only for compound **2aa** the MLCT1 is split into two components, which might be a result of a vibrational fine structure.

In conjunction with the above findings, one might expect to see two π–π^* transitions occurring within the β-diketonate ligand. In most compounds, one of them is easily recognized between 240 and 340 nm, because it shows about the same β-substituent dependency as the MLCT1 and MLCT2 bands (vide infra). This band is not affected by solvatochromic effects in accord with its assignment as a π–π^* transition. The second band is usually hidden under solvent absorptions (CH_2Cl_2) but may be seen for the phenyl-containing complexes. For these compounds, which exhibit rather low-lying π–π^* bands, a second strong band is found at ca. 5900 ± 650 cm^{-1} higher energy as the other (see Figure 2). The fact that this value of 5900 cm^{-1} matches that of the difference between the MLCT1 and MLCT2 bands (5200 cm^{-1}) nicely corroborates our assignments.

Table XII. Increments for the Calculation of Electronic Transitions in **2**[a]

$\lambda_{max} = K + \Delta(R^1) + \Delta(R^2)$

constants	π–π^* (1)	π–π^* (2)	MLCT1	MLCT2
K	40 850	35 650	26 350	22 400
$\Delta(CF_3)$	−1950	−900	−3350	−3450
$\Delta(Ph)$	−2350	−3150	−1700	−2450
$\Delta(OR)$	+2350	+2400	+4950	+3500
r[b]	1[c]	0.989[d]	0.993	0.998

[a] All data in cm^{-1}. The increments of Me and tBu were considered identical and constrained to zero. [b] Correlation coefficient derived from the 12 data (unless stated otherwise) for **2** measured in CH_2Cl_2. [c] Derived from the four phenyl-containing compounds (**2by**/**2yb**). [d] Compound **2aa** was omitted for this calculation.

An additional band was found in most complexes (frequently obscured) at a remarkably constant energy of 29 900 ± 300 cm^{-1} (≈335 nm). This band is not sensitive to solvent influences or to changes of the β-substituents in **2**. A similar band is found in the parent tungsten hydride **1** at 345 nm, and we think therefore that it may be a principal d–d transition. Other transition metal β-diketonates also show little dispersion of the ligand field splitting parameter on changing the β-substituents.[20]

The weak bands observed for the malonates **2dd** and **2ee** at ca. 400 nm may be assigned to an additional d–d transition.

Just as for the ^1H and ^{13}C NMR data of the β-diketonates may the various transitions be described as a summation of group-specific increments (Table XII). The calculated increments could not be successfully correlated to Hammett type parameters,[17] but they still obey the expected trends.[20] Thus, replacing a methyl group by a phenyl group shifts all the transitions to lower energy, mainly as a result of a conjugative lowering of the π^* levels of the β-diketonate moiety. The CF_3 group has a similar effect, but in contrast it destabilizes the t_{2g} level. On the other hand, the alkoxy substituent stabilizes the t_{2g} level but destabilizes the π^* levels.

(d) Mass Spectra. EI mass spectra of all compounds (Table S3, supplied as supplementary material) were measured under relatively constant conditions, i.e. with a 70-eV ion source at slightly elevated temperatures, and may therefore be compared. Some interesting generalizations can be made. Thus, the detected inorganic fragments always contained at least a tungsten atom and a PMe_3 group. The most abundant fragment usually was the $[M^+ - 28]$ peak, due to facile loss of CO from the parent molecule. The $[M^+]$ peak was usually present with somewhat lower abundancy. A signal due to loss of CO + Me (from PMe_3) $[M^+ - 43]$ is of relatively low but constant abundance throughout all compounds. A low abundance signal due to loss of PMe_3, $[M^+ - 76]$, is seen for most complexes, except for the CF_3-containing ones. The signals due to loss of CO + PMe_3, $[M^+ - 104]$, and of CO + NO + PMe_3, $[M^+ - 134]$, are observed for most species, except for those carrying alkoxy groups. The abundance of the $[M^+ - 104]$ peak is very irregular; vide infra.

Some fragments are characteristic for specific β-substituents. For compounds containing two different substituents, it was found that the characteristic fragmentation pattern of one group seems to completely "suppress" that of the other. This results in a kind of group priority reflecting the ease for cleavage from the β-diketone moiety, with OR > CF_3 > Ph > Me, tBu. Thus, when an alkoxy group is present (**2ae**/**2ea**, **2be**/**2eb**, **2cd**/**2dc**, **2dd**, **2ee**), one always detects the tungsten alkoxides $W(OR)(NO)(PMe_3)^+$, $W(OR)(NO)(PMe_3)_2^+$, and sometimes $W(OR)(PMe_3)^+$. When the molecule contains a CF_3 group (but no alkoxy group, as in **2aa**, **2ab**/**2ba**, and **2ac**/**2ca**), the tungsten fluorides WF(NO)-

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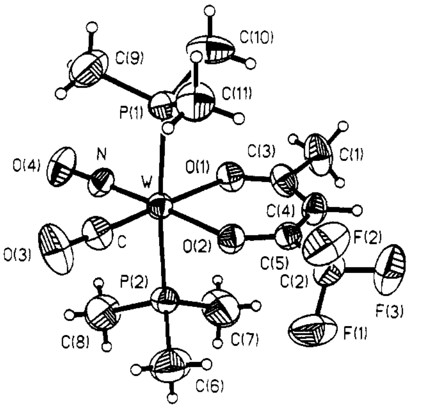

Figure 3. Molecular structure of **2ac**.

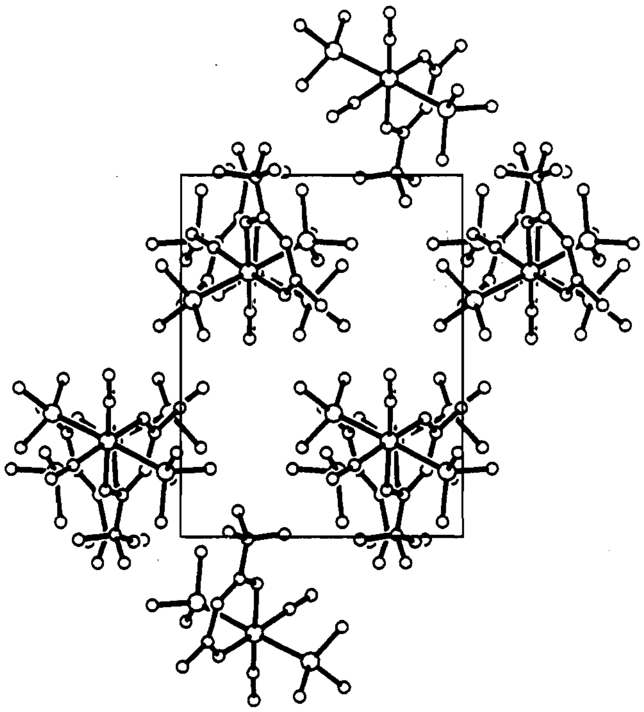

Figure 4. Molecular packing of **2ac** viewed down the *c* axis.

$(PMe_3)^+$ and $WF_2(NO)(PMe_3)^+$ are observed. When the molecule contains a phenyl group (**2bb** and **2bc**/**2cb**), the tungsten hydroxide $W(OH)(NO)(PMe_3)^+$ is observed, and when only alkyl groups are present (**2cc** and **2ff**), a $W(OH)_2(NO)(PMe_3)^+$ peak appears in addition. Interestingly, if one goes down the group priority list, the relative abundance of the $[M^+ - 104]$ peak increases.

(e) X-ray Structure of 2ac. The solid-state structure of **2ac** is depicted in Figure 3; its molecular packing, in Figure 4. Bond distances and angles are listed in Table XIII and XIV, respectively. The molecule, which resides as a discrete monomer in the crystal lattice, exhibits an almost octahedral coordination around tungsten. A minor distortion is caused by the β-diketonate ligand, which enforces an acute O(1)–W–O(2) angle of 83.0 (2)°. The two PMe_3 ligands are trans to each other (∠P(1)–W–P(2) = 174.8 (1)°). The plane perpendicular to the P–W–P′ axis contains the O,O′-coordinated β-diketonate ligand and the CO and NO ligands. As mentioned before, the NO ligand is located quasi trans to the CF_3 group, which identifies it as isomer **2ac** and not **2ca**. The two W–O bond lengths in **2ac** are virtually identical, 2.143 (6) (trans-CO) and 2.147 (5) Å (trans-NO), and in this sense they may be compared with those in other compounds of the type $W(CO)(NO)(PR_3)_2(\eta^2\text{-}O,O'\text{-ligand})$. In both $W(CO)(NO)(PMe_3)_2(\text{salicylate})$[1b] and $W(CO)(NO)(PPh_3)_2(O_2CMe)$[7] the trans-NO W–O bonds are somewhat shorter than the trans-CO ones (2.111 (7) vs 2.158 (7) and 2.217 (5) vs 2.249 (5) Å, respectively); however, differences are very small (6σ). In the two isomers of $W(CO)(NO)(PMe_3)_2(\eta^2\text{-}C,O\text{-}C(CO_2tBu){=}CHCO_2tBu)$ the W–O(keto) distances trans to NO as well as trans to CO are virtually identical (2.229 (6) and 2.223 (7) Å, respectively).[8] A discussion of the hybridization of the O atom on the basis of W–O bond lengths seems therefore rather tedious. On the other hand, the different C–C bond lengths in the β-diketonate ligand of **2ac** (1.41 (1) and 1.36 (1) Å) suggest some degree of localized enolate character on the CF_3 side, consistent with the supposed electronic properties; however, the similar C–O bond lengths (1.269 (9) and 1.280 (9) Å) suggests the opposite.

Table XIII. Selected Bond Lengths (Å) for **2ac**

W–P(1)	2.492 (3)	O(1)–C(3)	1.269 (9)
W–P(2)	2.494 (3)	O(2)–C(5)	1.280 (9)
W–O(1)	2.143 (6)	O(3)–C	1.17 (1)
W–O(2)	2.147 (5)	O(4)–N	1.237 (9)
W–N	1.790 (7)	C(1)–C(3)	1.53 (2)
W–C	1.920 (9)	C(2)–C(5)	1.52 (1)
$(P–C)_{av}$	1.81 (2)	C(3)–C(4)	1.41 (1)
$(F–C(2))_{av}$	1.323 (8)	C(4)–C(5)	1.36 (1)

Table XIV. Selected Bond Angles (deg) for **2ac**

P(1)–W–P(2)	174.8 (1)	$(W–P–C)_{av}$	115 (2)
P(1)–W–O(1)	87.2 (2)	$(C–P–C)_{av}$	103.1 (8)
P(1)–W–O(2)	88.8 (2)	W–O(1)–C(3)	131.5 (6)
P(1)–W–N	92.2 (2)	W–O(2)–C(5)	127.9 (6)
P(1)–W–C	89.7 (3)	W–N–O(4)	177.8 (6)
P(2)–W–O(1)	89.6 (2)	W–C–O(3)	177.4 (9)
P(2)–W–O(2)	86.8 (2)	$(F–C(2)–F)_{av}$	105.6 (5)
P(2)–W–N	92.3 (2)	$(C(5)–C(2)–F)_{av}$	113 (1)
P(2)–W–C	93.1 (3)	O(1)–C(3)–C(1)	117.7 (8)
O(1)–W–O(2)	83.0 (2)	O(1)–C(3)–C(4)	124.0 (8)
O(1)–W–N	100.0 (3)	C(1)–C(3)–C(4)	118.3 (7)
O(1)–W–C	172.9 (3)	C(3)–C(4)–C(5)	124.8 (7)
O(2)–W–N	176.9 (3)	O(2)–C(5)–C(2)	111.8 (8)
O(2)–W–C	90.5 (3)	O(2)–C(5)–C(4)	128.7 (8)
N–W–C	86.5 (3)	C(2)–C(5)–C(4)	119.5 (7)

Conclusions

The tungsten hydride **1** reacts with a wide variety of β-diketones by primary insertion of the most electron-deficient C=O bond (having the most electron-withdrawing group on that side, in the order CF_3 > Ph ≈ Me > OR) into the W–H bond of **1**, affording the intermediate **3** (only observed for β-diketones bearing a CF_3 group). Usually, a second equivalent of β-diketone substitutes the reduced β-diketone and a coordinated CO molecule, yielding the tungsten(0) β-diketonates **2** and the organic product β-hydroxy ketone. It is noted that the regioselectivity in these reductions approaches that of living systems in certain cases (baker's yeast). We are currently investigating the possibilities of modifying the tungsten hydride **1** with chiral auxiliaries in order to induce stereoselectivity as well.

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Supplementary Material Available: Tables of bond lengths and angles and thermal parameters for **2ac**, ^1H and ^{13}C NMR data for β-diketone reduction products (Tables S1 and S2), and mass spectral fragmentation patterns of **2** (Table S3) and tables listing details concerning the regression analyses of spectroscopic data on **2** (24 pages). Ordering information is given on any current masthead page.