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Photochemically Initiated Oxidative Carbon–Carbon Bond-Cleavage Reactivity in Chlorodiketonate Ni^{II} Complexes

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Abstract: Three mononuclear Ni^{II} complexes containing a 2-chloro-1,3-diketonate ligand and supported by the 6-Ph_2TPA chelate, as well as analogues that lack the 2-chloro substituent on the β-diketonate ligand, have been prepared and characterized. Upon irradiation at 350 nm under aerobic conditions, complexes containing the 2-chloro-substituted ligands undergo reactions to generate products resulting from oxidative cleavage, α-cleavage, and radical-derived reactions involving the 2-chloro-1,3-diketonate ligand. Mechanistic studies suggest that the oxidative cleavage reactivity, which leads to the production of carboxylic acids, is a result of the formation of superoxide, which occurs through reaction of reduced nickel complexes with O_2. The presence of the 2-chloro substituent was found to be a prerequisite for oxidative carbon–carbon bond-cleavage reactivity, as complexes lacking this functional group did not undergo these reactions following prolonged irradiation. The approach toward investigating the oxidative reactivity of metal β-diketonate species outlined herein has yielded results of relevance to the proposed mechanistic pathways of metalloenzyme-catalyzed β-diketonate oxidative cleavage reactions.

Keywords: diketones · dioxygenase · iron · nickel · oxygen · redox chemistry · superoxides

Introduction

Reaction pathways leading to the oxidative cleavage of the aliphatic carbon–carbon bonds of β-diketonate-type molecules are of current interest due to the identification of enzymes that catalyze the cleavage of these strong bonds.[1] Of primary interest toward better understanding the chemistry of such systems is the elucidation of how changes in the nature of the metal center, or the structural and/or electronic features of the β-diketonate, influence the reaction mechanism. An example of a metalloenzyme of this class is acireductone dioxygenase (Ni–ARD), which uses a mononuclear Ni^{II} center as a Lewis acid to stabilize a dianionic form of the acireductone substrate in a β-diketonate-type coordination motif (Scheme 1 (top)).[2] The acireductone dianion acts as a reductant toward O_2. Transfer of two electrons from the enediolate to O_2 is proposed to occur through an initial single-electron transfer to form superoxide and an organic radical, followed by collapse of the radical pair by attack of superoxide at the terminal carbon to yield an organoperoxo species. Attack of the terminal oxygen of the peroxo moiety at the other carbonyl produces a five-membered dioxetane ring from which aliphatic oxidative carbon–carbon bond cleavage and CO release is proposed to occur.

A different reaction pathway is proposed for the Fe^{II}-containing acetylacetone dioxygenase Dke1, which catalyzes the oxidative decomposition of acetylacetone to acetate and methyl glyoxal.[3] Kinetic studies suggest that the role of the Fe^{II} center is to help overcome the spin forbidden nature of the reaction between triplet dioxygen and the singlet substrate by delocalization of electron density through orbital mixing of the HOMOs of the β-diketonate and Fe^{II} center (Scheme 1 (bottom)). Electron transfer from the coordinated β-diketonate is suggested to occur in a concerted fashion with C–O bond formation at C(2) to give a peroxide species from which carbon–carbon bond cleavage occurs. It should be noted that replacing Fe^{II} in Dke1 with other divalent metal ions, including Ni^{II}, results in a loss of catalytic activity.[4] In model studies of relevance to Dke1, Limberg et al. have shown that although [Tp*Fe(acac)] (Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borato, acac = acetylacetonate) does not undergo reaction with O_2 to give products of acetylacetonate oxidative cleavage, a structurally similar complex of the more electron-rich diethylphenylmalonate β-diketonate, [Tp*Fe(Phmal)] (Phmal = diethyl phenylmalonate), undergoes O_2-dependent carbon–carbon bond-cleavage to give Dke1-type products (ethyl benzoylformate, ethoxide, and CO_2 through decomposition of $EtOCO_2^-$).[5] Control studies indicate that the formation of an Fe^{III} superoxide species is necessary in this model system for the observed reactivity. In a very recent study of relevance to Dke1, Nunes et al.

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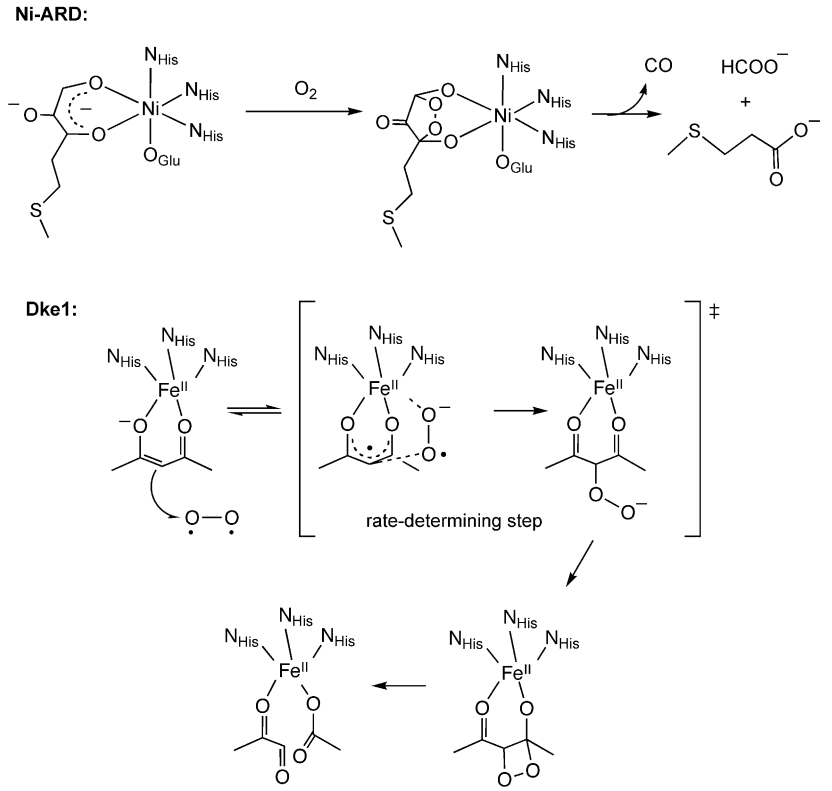


Scheme 1. Reactions catalyzed by Ni–ARD and Dke1.

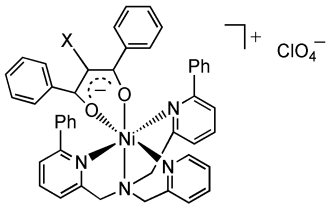
have reported the formation of $[Ni(en)_2(CH_3CO_2)][PF_6]$ (en = ethylenediamine) through treatment of $[Ni(acac)_2(H_2O)_2]$ with ethylenediamine in aerobic, aqueous solution. The oxidative cleavage of $acac^-$ to give acetate is suggested to involve superoxide generated in the reaction mixture, however no further details were provided.[6]

As can be seen in the chemistry of Ni–ARD, Dke1, and related model systems, specific combinations of β-diketonate ligand and metal ion impart oxidative carbon–carbon bond-cleavage reactivity. In Ni–ARD, a typically redox-inactive metal center stabilizes the dianionic form of a β-diketonate-type substrate having inherent reductive reactivity toward O_2. In Dke1, a potentially redox-active Fe^{II} center is partnered with the O_2-stable acetylacetone substrate. In this latter case, the metal center is important for redox reactivity with O_2 to initiate the oxidative cleavage process.

We have previously shown that the β-diketonate complex $[(6\text{-}Ph_2TPA)Ni(PhC(O)C(OH)C(O)Ph)][ClO_4]$ (**1**, Figure 1) reacts with O_2 to give products (carboxylates and CO) akin to those generated in the Ni–ARD-catalyzed reaction.[7] The mechanism by which this occurs involves two-electron oxidation of the enediolate moiety to give an intermediate triketone species that subsequently undergoes reaction with HOO^-, generated in the reaction mixture, to give aliphatic carbon–carbon bond-cleavage products.[8] Although this mechanism differs from that proposed for the enzyme[1], this system does mimic Ni–ARD in terms of incorporating the combination of an inherently O_2-reactive β-diketonate ligand with a redox-inactive Ni^{II} center.

Complexes that are structurally similar to **1** but instead have an unsubstituted β-diketonate ligand, such as $[(6\text{-}Ph_2TPA)Ni(PhC(O)CHC(O)Ph)][ClO_4]$ (**9**), are stable with respect to O_2 under ambient conditions.[7] As described herein, Ni^{II} complexes having a mildly electron-withdrawing chloride at the C(2) position, for example, $[(6\text{-}Ph_2TPA)Ni(PhC(O)C(Cl)C(O)Ph)][ClO_4]$ (**6**), are also stable with respect to O_2 under ambient conditions. The lack of dioxygen reactivity for **6** and **9** is not unexpected because the reduced electron density within the π system of the β-diketonate moiety makes these anions poorer reducing agents than the α-hydroxy-containing analogue.

Previous studies[9] of the photochemistry of Ni^{II} β-diketonate species led us to consider how this approach might be used to induce redox activity at the nickel center of **6** and **9** as a means toward promoting oxidative carbon–carbon bond-cleavage reactivity. It is known, for example, that $[Ni(acac)_2]$ undergoes photoreduction to produce transient Ni^I complexes in the presence of stabilizing ligands.[9] Based on this literature precedent, if Ni^I β-diketonate species can be photochemically generated, starting from complexes, such as **6** and **9**, this offers the possibility of producing a combination of a Ni^I center and a β-diketonate radical. The Ni^I could then activate O_2 to generate Ni^{II} and O_2^-, from which subsequent oxidative chemistry may occur.[10] This net transfer of one electron from the β-diketonate to O_2 would be similar to the mechanism proposed for the Dke1 enzyme, in which the ligand is also oxidized by



1, X = OH
6, X = Cl
9, X = H

Figure 1. Synthetic complex studied as a model system for Ni^{II}-contaning acireductone dioxygenase **1** and analogues **6** and **9** that are O_2-stable under ambient conditions.

one electron to form superoxide, albeit in the nickel case this would involve direct electron transfer rather than orbital mixing.

Herein, we outline the results of studies into the photochemical reactivity of **6** and **9** and *para*-substituted analogues. The results show that oxidative cleavage products are generated for systems containing a 2-chloro substituent on the coordinated enolate.

Results and Discussion

Preparation of 2-chloro-1,3-diones: β-diketones can be chlorinated at the α position by using various reagents.[11] Recent studies in this area have focused on the use of hypervalent iodine reagents[12] and reactions performed by using *N*-chlorosuccinimide in an ionic liquid[13] or CCl_4.[14] In a new synthetic route (Scheme 2 (top)), we have found that treatment of the appropriate β-diketone (**2a**–**2c**) with $RuCl_3$/Oxone/H_4NCl in CH_3CN/H_2O/EtOAc gives the 2-chloro compounds (**3a**–**3c**) as crystalline solids in high purity, following recrystallization(s).

Complex synthesis and characterization: A series of mononuclear Ni^{II} 2-chloro-1,3-diketonate complexes (**4**–**6**) supported by the 6-Ph_2TPA ligand were prepared as outlined in the bottom equation in Scheme 2. Crystalline solids were isolated in yields greater than 70%. For reactivity comparison, structurally similar β-diketonate complexes lacking the 2-chloro substitutent (**7**–**9**) were generated. We note that complex **9** has been reported previously.[7] Each new complex was characterized by elemental analysis, IR, ^{1}H NMR, and UV/Vis spectroscopy, and in some cases, mass spectrometry and/or X-ray crystallography.

Single-crystal X-ray structures were obtained for **5**, **6**, and **8**. Details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are given in Table 2. These complexes all contain a pseudo-octahedral Ni^{II} cation with bidentate coordination of the corresponding β-diketonate (Figure 2 and Figure S1 in the Supporting Information). Bond lengths within the six-membered chelate ring in each complex are typical for nickel β-diketonates.[7] The C–Cl bond lengths in **5** and **6** are within the range previously reported for metal-bound 2-chloro-1,3-diketonates (1.68–1.81 Å), being particularly close to that reported for

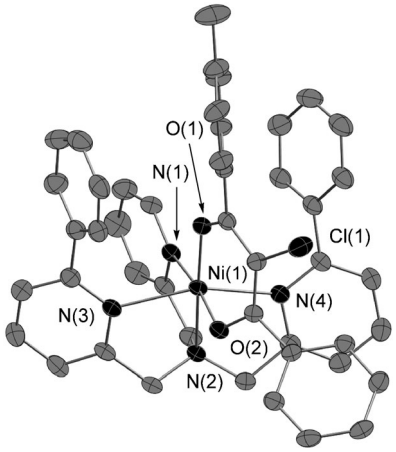
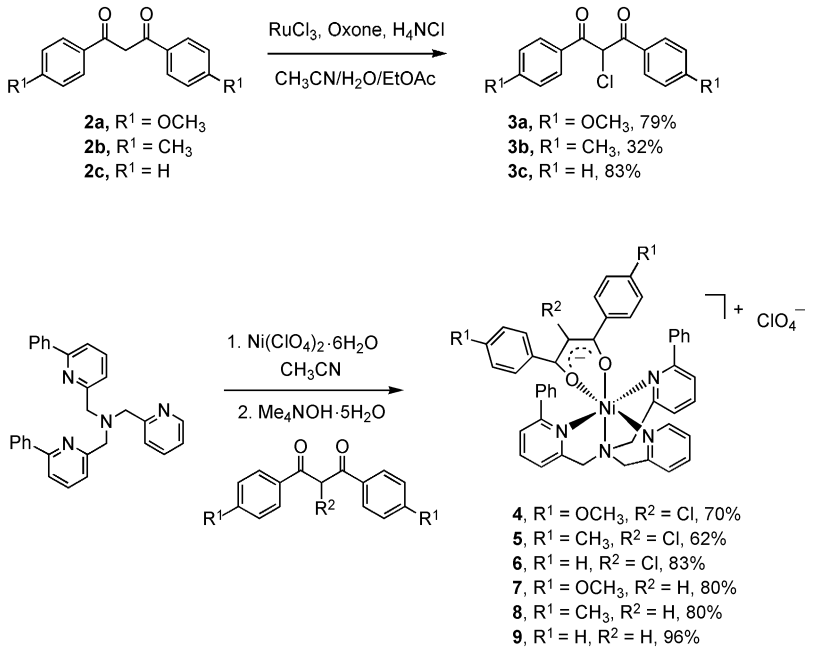


Figure 2. Thermal ellipsoid representation of the cationic portion of **5**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.



Scheme 2. Synthesis of 2-chloro-1,3-diones (top) and Ni^{II} 2-chloro-1,3-diketonate complexes supported by the 6-Ph_2TPA ligand (bottom).

Cu^{II} complexes (1.739(3) and 1.755(3) Å).[15] As can be seen in Table 2, there are only subtle changes in the Ni–N/O bond lengths as the nature of the substituents on the β-diketonate is changed. Comparison of the structural features of **6** to those of **1** (Figure 1) revealed that the Ni–N_{PhPy} bonds are slightly elongated in the 2-hydroxy-1,3-diketonate complex relative to those found in 2-chloro analogue **6** (Ni–N_{PhPy}, **1**: av. 2.30 Å; **6**: av. 2.25 Å).

Selected spectroscopic data for **4**–**9** is given in Table 3. Each β-diketonate complex has an absorption feature at ≈370 nm that may be assigned as a $\pi \rightarrow \pi^*$ transition involving the β-diketonate ligand. Comparison of the 2-chloro-1,3-diketonate

Table 1. Crystallographic data for **5**, **6**, and **8**.

	5·$C_4H_{10}O$	**6**	**8**·2 CH_2Cl_2
formula	$C_{47}H_{40}Cl_2N_4NiO_6$·$C_4H_{10}O$	$C_{45}H_{36}Cl_2N_4NiO_6$	$C_{49}H_{41}ClN_4NiO_6$·2 CH_2Cl_2
M_r	960.56	858.39	1021.85
T [K]	150(1)	150(1)	150(1)
crystal size [mm]	0.30×0.28×0.20	0.38×0.15×0.13	0.30×0.22×0.12
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.96810(10)	9.7136(1)	13.5383(2)
b [Å]	13.6006(2)	13.2959(2)	17.0153(2)
c [Å]	16.1278(3)	16.7754(3)	23.0279(3)
α [°]	108.5037(6)	77.5113(7)	97.2779(7)
β [°]	104.6479(9)	76.7675(10)	92.9850(7)
γ [°]	102.9892(9)	68.7334(9)	112.8856(7)
V [Å^3]	2271.55(6)	1944.11(5)	4817.82(11)
Z	2	2	4
ρ_{calcd} [g cm^{-3}]	1.404	1.466	1.409
μ [mm^{-1}]	0.603	0.693	0.733
$F(000)$	1004	888	2112
Θ range [°]	1.91–27.48	2.34–27.49	1.71–27.44
index ranges	$-14 \le h \le 15$ $-17 \le k \le 17$ $-20 \le l \le 20$	$-12 \le h \le 12$ $-17 \le k \le 17$ $-21 \le l \le 21$	$-16 \le h \le 17$ $-22 \le k \le 21$ $-29 \le l \le 29$
reflns collected	19512	16726	40512
unique reflns	10319 (R_{int}=0.0235)	8901 (R_{int}=0.0237)	21813 (R_{int}=0.0420)
R_{int}	0.0235	0.0237	0.0420
data/restr./param.	10319/24/632	8901/0/533	21813/12/1184
GoF (F^2)	1.024	1.027	1.026
R_1, wR_2 [$I > 2\sigma(I)$]	0.0427, 0.1055	0.0364, 0.0816	0.0497, 0.1106
R_1, wR_2 (all data)	0.0617, 0.1163	0.0553, 0.0889	0.0944, 0.1293
max/min transmission	0.8889/0.8398	0.9153/0.7786	0.9172/0.8101
$\Delta\rho_{(max/min)}$ [eÅ^{-3}]	0.441/−0.664	0.333/−0.510	0.0820/−0.862

complexes (**4–6**) with their unsubstituted analogues (**7–9**) revealed a redshift of 4 nm for the former.

The ^{1}H NMR features of **1** and **9** have been reported previously.[7,16] Resonances in selected regions of the ^{1}H NMR spectra of **4–6**, **7** and **8** can be assigned on the basis of chemical shift, integrated intensity, and comparison to previously studied complexes.[7,16,17] All of the complexes (**4–9**) exhibit C_s symmetry in CD_3CN on the NMR time scale, as shown by the presence of only two resonances for the β′ pyridyl protons (Figure 3), indicating that the phenyl-appended pyridyl rings are equivalent. Diagnostic resonances for the pyridyl-ring β-H's and phenyl-appended pyridyl-ring β′-H's (Figure 3) are found in the region of $\delta = 44$–48 ppm (Table 3). The effect of changing the *para*-substituent on the aryl groups of the β-diketonate ligand can be seen in the shift of the pyridyl γ-H's in the two series **4–6** and **7–9**, and in a shift of the β-diketonate methyne proton in **7–9**. In the latter set of complexes, the pyridyl β, β′, and γ proton resonances are shifted upfield by $\delta = 1$–2 ppm relative to the 2-chloro analogues.

Reactivity studies: It was found that the yellow color of solutions of the 2-chloro-1,3-diketonate complexes **4–6** in acetonitrile faded ($\lambda_{irr} = 350$ nm) over the course of several hours under aerobic conditions upon exposure to UV light. As shown in Figure 4 for methoxy-substituted compound **4**, this corresponds to loss of the $\pi \rightarrow \pi^*$ absorption band of the β-diketonate at 378 nm. An isosbestic point for the reaction was identified at 269 nm.

The products of each aerobic photochemical reaction were determined after irradiating a 0.002 M solution of each complex (**4–6**) in acetonitrile at 350 nm for 20 h, under an aerobic atmosphere. The Ni^{II}-containing products were identified by using ^{1}H NMR spectroscopy (Figures 5–7) and ESI-MS. The most reactive compound was found to be methoxy derivative **4** (Figure 5). A major Ni^{II} product of this reaction is the chloride complex [(6-Ph_2TPA)Ni(Cl)(CH_3CN)][ClO_4] (**10**)[17], as shown by the presence of resonances at $\delta = 54$ and 37 ppm. Also present are resonances associated with a monoanisate complex [(6-Ph_2TPA)Ni{O_2C(*p*-$OCH_3C_6H_4$)}][ClO_4] (**11**) and the dianisate complex [(6-Ph_2TPA)Ni{O_2C(*p*-$OCH_3C_6H_4$)}$_2$] (**12**). Complexes **11** and **12** were independently synthesized and characterized to confirm the assignment. The formation of **10–12** in the photochemical reaction of **4** is also supported by ESI-MS investigations. From comparison of ^{1}H NMR spectra, it is evident that the aerobic photochemical reaction of **4** goes to completion over the 20 h irradiation period, as no signals for the starting material could be identified. A summary of the reaction of methoxy-substituted **4** is presented in Scheme 3.

The reaction of methyl-substituted **5** under aerobic conditions also leads primarily to the formation of chloro complex **10** (Figure 6).[17] The reaction of **6** (Figure 7) differs from that of **4** and **5** in that ^{1}H NMR resonances from the starting material are clearly evident in the ^{1}H NMR and ESI-MS spectra after 20 h of irradiation. Note that as a control, 0.002 M solutions of **4–6** in CD_3CN were stored in the dark under ambient aerobic conditions for sev-

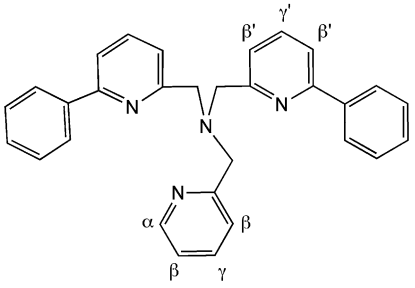


Figure 3. Labeling scheme for the 6-Ph_2TPA ligand.

Table 2. Selected bond lengths [Å] and angles [°].

	5·$C_4H_{10}O$	**6**	**8**·2 CH_2Cl_2
Ni(1)–N(1)	2.0569(18)	2.0404(15)	2.068(2)
Ni(1)–N(2)	2.0635(17)	2.0882(15)	2.085(2)
Ni(1)–N(3)	2.3041(17)	2.3174(15)	2.283(2)
Ni(1)–N(4)	2.2261(18)	2.1890(15)	2.238(2)
Ni(1)–O(1)	1.9709(14)	1.9748(12)	1.9796(16)
Ni(1)–O(2)	1.9968(14)	1.9883(13)	1.9885(17)
C(37)–C(38)	1.418(3)	1.422(3)	1.401(3)
C(38)–C(39)	1.411(3)	1.397(3)	1.405(3)
C(38)–Cl(1)	1.760(2)	1.7571(18)	–
O(1)-Ni(1)-O(2)	88.78(6)	89.13(5)	91.57(7)
O(1)-Ni(1)-N(1)	97.65(6)	94.17(6)	90.92(8)
O(2)-Ni(1)-N(1)	172.50(6)	176.66(6)	175.39(8)
O(1)-Ni(1)-N(2)	178.06(6)	174.91(5)	171.45(8)
O(2)-Ni(1)-N(2)	89.74(6)	93.15(6)	95.57(7)
N(1)-Ni(1)-N(2)	83.91(7)	83.51(6)	82.29(8)
O(1)-Ni(1)-N(4)	100.33(6)	102.77(5)	103.07(8)
O(2)-Ni(1)-N(4)	85.78(6)	92.08(5)	93.47(7)
N(1)-Ni(1)-N(4)	96.80(7)	87.69(6)	82.18(8)
N(2)-Ni(1)-N(4)	78.31(7)	81.71(6)	81.23(8)
O(1)-Ni(1)-N(3)	101.07(6)	98.63(5)	100.47(7)
O(2)-Ni(1)-N(3)	94.50(6)	84.69(5)	82.25(7)
N(1)-Ni(1)-N(3)	80.52(7)	94.29(6)	101.11(8)
N(2)-Ni(1)-N(3)	80.30(7)	77.08(6)	75.92(8)
N(4)-Ni(1)-N(3)	158.60(7)	158.31(6)	156.18(7)
O(1)-Ni(1)-O(2)	88.78(6)	89.13(5)	91.57(7)
O(1)-Ni(1)-N(1)	97.65(6)	94.17(6)	90.92(8)
O(2)-Ni(1)-N(1)	172.50(6)	176.66(6)	175.39(8)
O(1)-Ni(1)-N(2)	178.06(6)	174.91(5)	171.45(8)
O(2)-Ni(1)-N(2)	89.74(6)	93.15(6)	95.57(7)
N(1)-Ni(1)-N(2)	83.91(7)	83.51(6)	82.29(8)
O(1)-Ni(1)-N(4)	100.33(6)	102.77(5)	103.07(8)
O(2)-Ni(1)-N(4)	85.78(6)	92.08(5)	93.47(7)
N(1)-Ni(1)-N(4)	96.80(7)	87.69(6)	82.18(8)

Table 3. Selected spectroscopic features for **4**–**9**.

	4	**5**	**6**	**7**	**8**	**9**
λ_{max} [nm][a]	378	374	372	374	370	368
ε [10^4 м$^{-1}$ cm^{-1}]	1.03	1.16	0.80	2.38	2.16	1.30
β-py[b]	48.4	48.1	48.4	46.0	47.0	46.6
	42.8	43.5	43.5	44.1	44.4	44.1
β′-py	46.0	46.0	46.4	44.1	44.1	44.9
	34.8	34.6	34.7	33.8	33.9	34.3
γ-py	15.4	15.5	15.5	14.9	15.0	15.1
α-CH	–	–	–	−14.1	−13.9	−13.6

[a] UV/Vis spectra obtained in CH_3CN. [b] ^{1}H NMR spectra obtained in CD_3CN at ambient temperature at 400 MHz. Chemical shifts are reported in ppm.

eral days and produced no decomposition products, as determined by ^{1}H NMR spectroscopy.

For each reaction described above, the organic products could not be analyzed in the presence of the Ni^{II} complex(es). Therefore, these products were separated by filtration of each reaction mixture through a short silica plug using ethyl acetate as the eluent. Each sample was analyzed by ^{1}H NMR spectroscopy and GC-MS. The amount of organic material isolated from each reaction mixture corresponds to >80% by mass of that expected from the respective starting 2-chloro-1,3-diketonate ligand. Control reactions indicate that the coordinated 1,3-diketonate ligand in

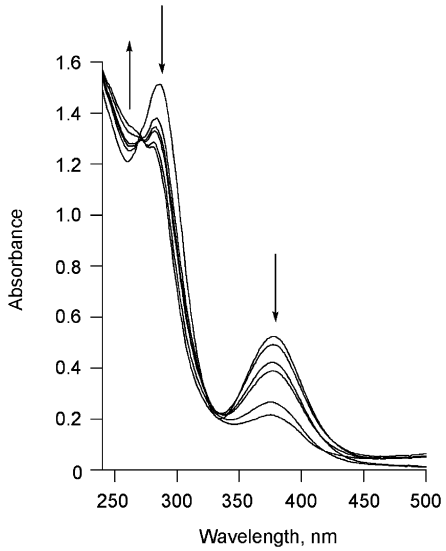


Figure 4. Absorption changes over time observed for the aerobic photochemical reaction of **4**.

4–**6**, and the anisate ligands in **11** and **12**, are released upon passage of the complexes through the silica plug. Thus, the presence of 2-chloro-1,3-dione in the organic products is further evidence for incomplete reactions. The inorganic residue on the silica is eluted by washing with acetonitrile, followed by methanol. ^{1}H NMR analysis of the inorganic fractions showed the presence of $[(6\text{-}Ph_2TPA)Ni(CH_3CN)_2][ClO_4]_2$ (**13**, Figure 5), which was not present in the reaction mixtures prior to work-up.

Upon irradiation of **4** for 20 h under aerobic conditions, the primary organic product generated is *para*-anisic acid (**I**, Figure 8), along with lesser amounts of *para*-anisil methyl ketone (**II**), anisaldehyde, deoxyanisoin (**III**), and halogenated species (for example, 2-chloro-1-(4-methoxyphenyl)propan-1-one; Figure 8 (top)). Notably, performing the same reaction with **4** under N_2 results in the formation of only α-cleavage products (for example **II** and **III**, Figure 8 (bottom)). Thus, oxygen is required for the generation of the carboxylic acid product.

The photoreactivity of the methoxy-substituted 2-chloro-1,3-dione **3a** has previously been evalutated by Kosmrlj et al.[18] After irradiation of a 0.002 м solution of the diketone at 350 nm for 2 h under aerobic conditions, they noted the formation of only α-cleavage products (Scheme 4). Thus, the presence of nickel is required for oxidative cleavage reactivity involving the 2-chloro-1,3-dione. The aerobic photochemical reaction involving the methyl-containing Ni^{II} 2-chloro-1,3-diketonate complex **5** results in the formation of multiple products (Figure 8) including flavone and deoxytoluoin, with lesser amounts of *para*-toluic acid, *para*-tolualdehyde and methyl-*para*-tolyl ketone. Under a N_2 atmosphere, the reaction involving **5** reached only approximately 80% completion. The organic products

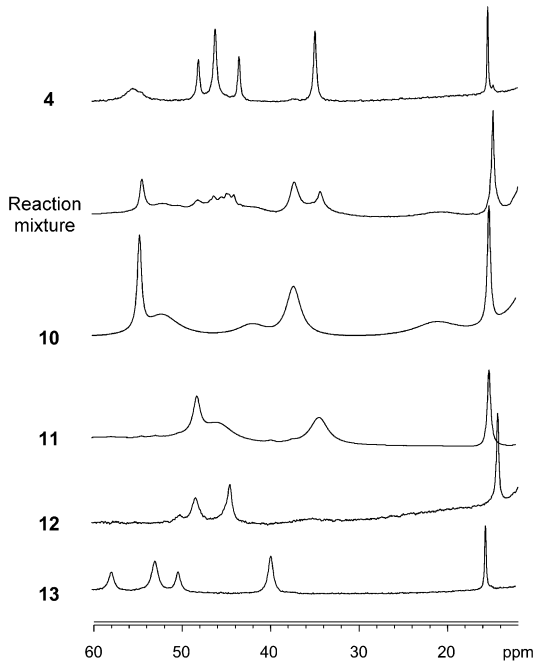


Figure 5. Selected features of the ^{1}H NMR spectra of analytically pure **4** and **10**–**13** and the reaction mixture produced upon irradiation of **4** under aerobic conditions at 350 nm for 20 h in CH_3CN. All spectra were obtained at 400 MHz in CD_3CN.

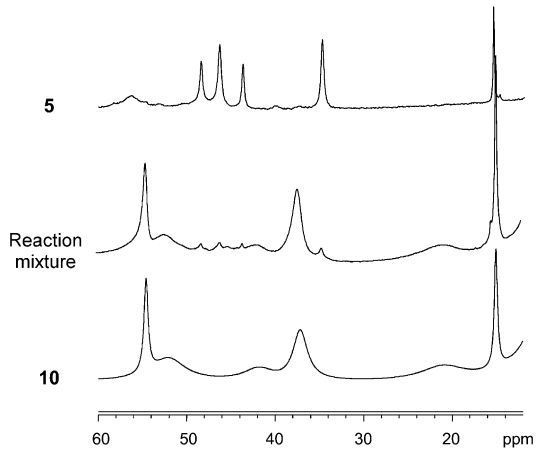
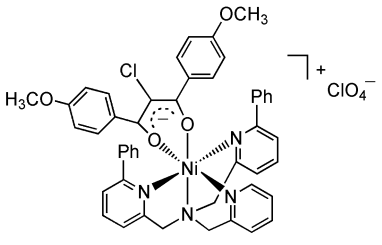
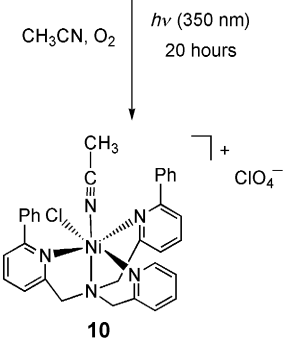
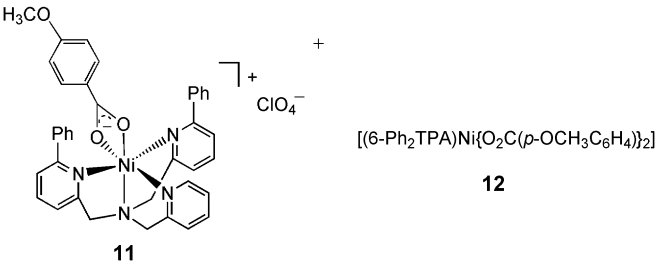


Figure 6. Selected features of the ^{1}H NMR spectra of analytically pure **5** and **10** and the reaction mixture produced upon irradiation of **5** under aerobic conditions at 350 nm for 20 h in CH_3CN. All spectra were obtained at 400 MHz in CD_3CN.

were a similar mixture to that found under aerobic conditions, except *para*-toluic acid is not generated. As the photoreactivity of the methyl-substituted **3b** had not previously been reported, we performed this reaction under the conditions previously employed for **3a** and **3c** (0.002 M in CH_3CN under aerobic conditions with irradiation at 350 nm for 2 h).[18] The primary reaction products generated were the α-cleavage products methyl-*para*-tolyl ketone and *para*-tolualdehyde, with no *para*-toluic acid.







Scheme 3. Ni^{II} complexes generated upon irradiation of **4** at 350 nm for 20 h in aerobic CH_3CN.

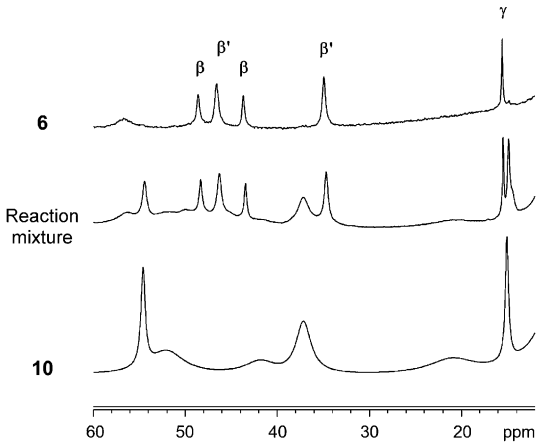


Figure 7. Selected features of the ^{1}H NMR spectra of analytically pure **6** and **10** and the reaction mixture produced upon irradiation of **6** under aerobic conditions at 350 nm for 20 h in CH_3CN. All spectra were obtained at 400 MHz in CD_3CN.

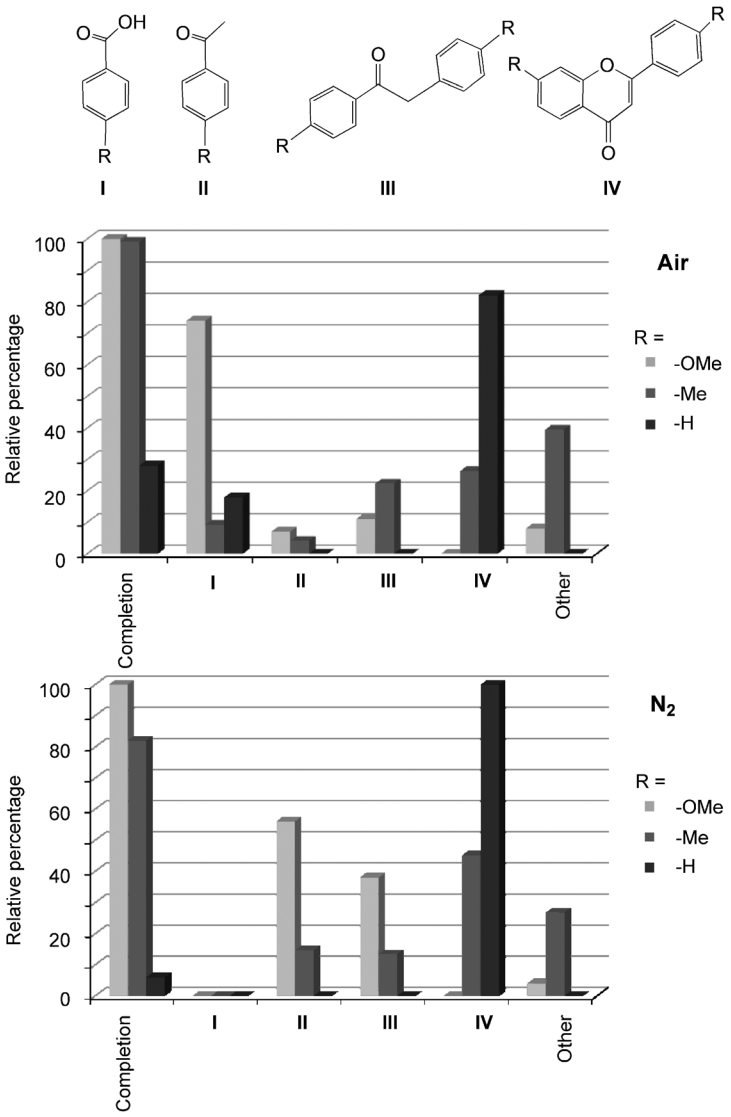


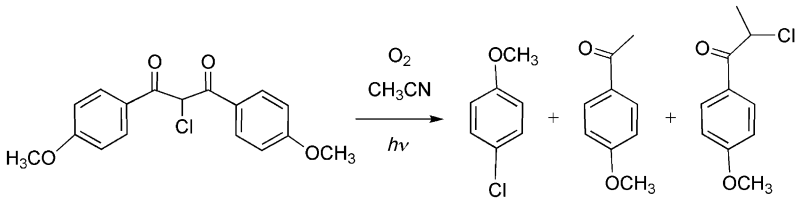
Figure 8. Top) Organic products generated in photochemical reactions of **4–6** under aerobic conditions with irradiation at 350 nm for 20 h in CH_3CN. Bottom) Products generated in the same reactions performed under N_2. In each graph the column labeled completion corresponds to the relative percentage of reaction completion observed after 20 h. The relative percentages of **I–IV** refer to the amount of product generated as a percentage of the overall amount of 2-chloro-1,3-diketonate that underwent reaction under the prescribed conditions. Other refers to species such as *para*-R-arylaldehyde, chloro-containing compounds, and unidentified compounds.

As noted above, the photochemical reaction of **6** under aerobic conditions does not go to completion after 20 h of irradiation at 350 nm. Hence, the major organic product isolated from the reaction mixture is the unreacted 2-chloro-1,3-dione **3c**. However, of the remaining organic compounds generated, flavone is the primary product (Figure 8), along with a small amount of benzoic acid. Performing the irradiation of **6** under a N_2 atmosphere resulted in less than 10% of the starting material undergoing reaction, with only trace amounts of flavone generated. Kosmrlj et al. previously reported that irradiation of unsubstituted 2-chloro-1,3-dione **3c** yielded the photocyclization product **IV** as the sole product in approximately 50% yield, regardless of conditions (air, argon or oxygen atmosphere).[18]

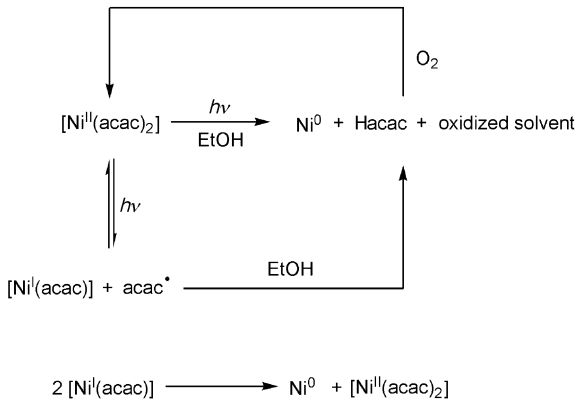
Complexes **7–9** were tested for photoreactivity under both aerobic and anaerobic conditions identical to those used for the 2-chloro-1,3-diketonate complexes **4–6**. Analysis of the product mixtures by ^1H NMR spectroscopy using paramagnetic parameters showed no change from the starting material.

Mechanistic experiments: The differing product distributions found for the reactions of **4–6** and the overall lack of reactivity found for **7–9** was evaluated through consideration of literature precedent and the results of additional mechanistic experiments. In pioneering work by Lintvedt et al., it was found that when $[Ni(acac)_2]$ is irradiated at 252 nm in ethanol in the absence of O_2, free Hacac is produced along with a colloidal suspension of Ni^0 or a Ni^0 film (Scheme 5).[19,20] The mechanism for reduction of the Ni^{II} center in $[Ni(acac)_2]$ is thought to involve a $\pi\rightarrow\pi^*$ transition to a vibrationally excited π^* state from which the reduction can take place. However, the involvement of ligand-to-metal charge transfer has also been proposed. In either scenario, an intial single-electron reduction of Ni^{II} to Ni^{I} can occur (Scheme 5).[9] The Ni^{I} formed could then react with a second Ni^{I} species in solution to disproportionate and form Ni^{II} and Ni^0. Interestingly, photochemical reduction of $[Ni(acac)_2]$ is not observed to occur in the presence of O_2.[19] However, this observed overall lack of reactivity may represent the sum of a photochemical reduction followed by rapid reoxidation of the reduced nickel and complexation to give $[Ni(acac)_2]$ (Scheme 5). This is consistent with the fact that the anaerobically generated photoreduction products of $[Ni(acac)_2]$ readily oxidize in O_2 to regenerate the starting material.[20]

Given the literature precedent described above, we hypothesize that low-valent nickel complexes, likely Ni^{I}, are generated upon photoirradiation of the 6-Ph_2TPA-ligated Ni^{II} β-diketonate complexes. Irradiation on the high-energy shoulder of the $\pi\rightarrow\pi^*$ transition that is present at 368–380 nm could



Scheme 4. α-Cleavage products formed from the photoirradiation of **3a** at 352 nm in aerobic CH_3CN for 2 h.[18]

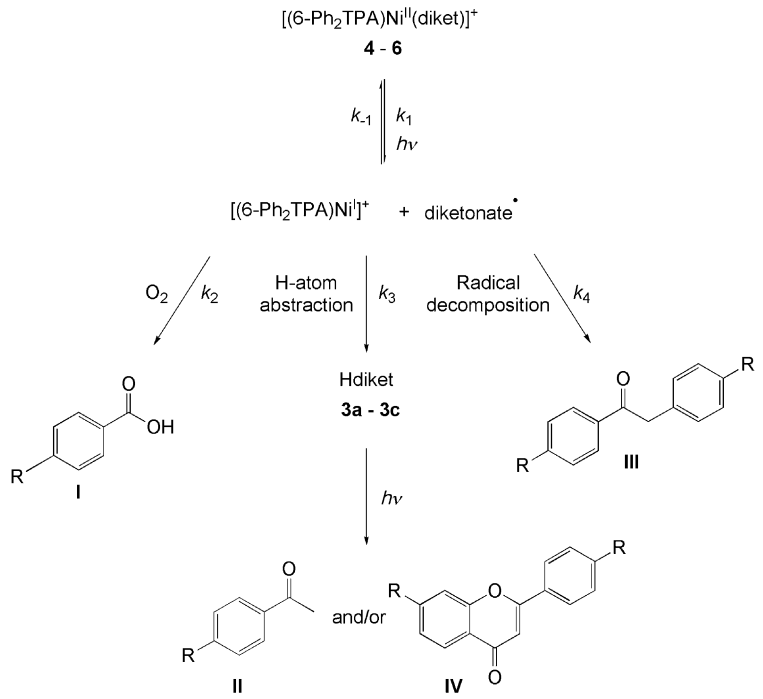


Scheme 5. Proposed reaction sequence for photoreduction of $Ni(acac)_2$.

produce a high-energy electronic state on the β-diketonate with reducing character, leading to one-electron reduction of Ni^{II} to Ni^{I} and the formation of a β-diketonate radical (Scheme 6). Although we cannot directly probe the Ni^{I}/β-diketonate radical species, cyclic voltammetry studies were performed to provide insight into the redox properties of the Ni^{II} 2-chloro-1,3-diketonate complex **4**, as well as an unsubstituted analogue **7**. Complex **4** exhibits two poorly reversible cathodic features at approximately −1.82 and −1.91 V versus Fc/Fc^+ (Figure S2 (top) in the Supporting Information), suggesting that an initially formed Ni^{I} β-diketonate anion species is susceptible to further reduction and/or a chemical reactivity that limits reversiblity. A new oxidative wave at −0.44 mV, generated after the cathodic scan, indicates the formation of a possibly electrode-deposited nickel species. Complex **7** exhibits a quasireversible cathodic wave at approximately −1.93 V (Figure S2 (bottom) in the Supporting Information), indicating that the stability of the Ni^{I} β-diketonate anion species is influenced by the nature of the enolate ligand. In the presence of O_2, solutions of **4** and **7** exhibit only a quasireversible cathodic wave consistent with the reduction of O_2 to O_2^{-}.[21] The reversibility of this feature improves in the absence of the complex, indicating that the electrochemically generated superoxide is reacting with the complex (either **4** or **7**). Notably, we have found that the Ni^{II} β-diketonate complexes **4** and **7** are reactive with potassium superoxide (solubilized by 18-crown-6) in acetonitrile. In the reaction of **4**, the carboxylic acid product (**I**) was detected as the major β-diketonate-derived product.

Literature precedent, as well as experimental evidence, suggests that the oxidative reactivity leading to carboxylic acid formation in the photoreactions of **4–6** likely involves the formation of a trione intermediate. Tada et al. have proposed that in situ generated α-I-β-diketones undergo reaction with O_2 upon irradiation with fluorescent light to produce 1,3-diphenylpropanetrione, PhC(O)C(O)C(O)Ph.[22] We have shown that the same trione is generated as a reactive intermediate upon reaction of **1** with O_2.[8] The trione is a transient intermediate that may then react with in situ generated peroxide to form the observed carboxylate cleavage products. Alternatively, triones with aryl groups in the C(1) and C(3) positions may undergo a Lewis acid promoted benzoyl migration and subsequent decarbonylation to form benzil (PhC(O)C(O)Ph), making the detection of benzil a potential probe for the detection of triketone intermediates. Careful examination of the products generated in the photoreaction of **6** (labeled as "other" in Figure 8) shows the presence of a small amount of benzil, strongly suggesting the formation of the triketone intermediate.[23]

To probe the formation of a trione intermediate, ^{18}O-labeling studies were undertaken and the results obtained for the aerobic photoreaction of **6** are consistent with previous reports. Specifically, the amount of benzoic acid containing one ^{18}O label (36%) is generally similar to that found for the reaction of **1** (≈50%).[8] Labeling studies were also undertaken to further explore the photoinduced oxidative cleavage reactivity of **4** under aerobic conditions. Irradiation of **4** in the presence of $^{18}O_2$ (99%) resulted in the isolation of a sample of



Scheme 6. Proposed photochemical reaction pathways for **4–6** leading to the formation of **I–IV** (diket = diketonate).

para-anisic acid that contains approximately 31% unlabeled O, 46% with one ^{18}O, and 23% with two ^{18}O atoms (Table S1 in the Supporting Information). We are cautious to avoid overinterpreting this labeling data in the absence of a more thorough kinetic analysis of the reactions. However, we tentatively propose that the observed formation of double-labeled anisic acid in the reaction of **4** could be a result of previously reported scrambling reactions in the presence of the electron-donating methoxy substituent.[24]

To gain additional insight into the effect of the *para*-substituent on the reactivity of the 2-chloro-1,3-diketonate ligands in **4–6**, the rates of the aerobic photoreactions were investigated and compared. Monitoring the change in absorbance at 378 nm (Figure 4) as a function of time for the photochemical reaction of **4** under aerobic conditions indicated a pseudo first-order process (Figure S3 in the Supporting Information). Similar experiments performed by using **5** and **6** demonstrated that the reaction slows in the order **4** > **5** > **6**. This is consistent with quantum yields measured for the reactions in which **4** (0.00038 ± 0.00002) > **5** (0.00032 ± 0.00003) > **6** (0.00020 ± 0.00007). Thus, enhanced electron density within the 2-chloro-1,3-diketonate ligand increases the quantum yield and the rate of the reaction. As shown in Scheme 6, the overall low quantum yield of these reactions may be attributed to recombination of the Ni^{I} species with the β-diketonate radical.

The formation of the other organic products (**II–IV**) in the photoreactions of **4–6** can be rationalized on the basis of the chemistry of the β-diketonate radical. The production of **II** and **IV** suggests that free neutral 2-chloro-1,3-dione is generated in the reaction mixture and subsequently undergoes the photochemical reactions previously reported by Kosmrlj et al.[18] The formation of free neutral **3a–3c** most likely occurs through hydrogen-atom abstraction reactivity involving the β-diketonate radical. Although we have not definitively identified the H-atom donor in the system, we have found that an aerobic photochemical experiment involving **4** in the presence of the H-atom donor 9,10-dihydroanthracene significantly increases the rate of disappearance of the 2-chloro-1,3-diketonate complex. The formation of **III** has not been reported in the photochemical reactions of **3a** and **3c**,[18] although it has been detected as a product in the photochemical reactions of dibenzoyldiazomethane, suggesting decomposition involving the β-diketonate radical.[25]

As depicted in Scheme 6, we propose that the observed rate of reaction for **4–6** will be influenced by the magnitude of the pseudo-first-order rate constants k_2, k_3, and k_4 as compared to k_{-1}. For example, the rate should increase in the presence of O_2 as the pathway represented by k_2 becomes operative. Addition of an H-atom donor compound, such as 9,10-dihydroanthracene, would also be expected to increase the rate, as the magnitude for k_3 would increase and k_2 may also increase due to the ability of a hydrogen-atom donor to trap a nascent superoxide radical. The relative rates of reaction for **4** under an aerobic or nitrogen atmosphere (Figure S4 in the Supporting Information) and in an aerobic mixture containing 9,10-dihydroanthracene were determined and qualitatively support the proposed reaction scheme. The reactivity trend **4** > **5** > **6** described earlier can be explained either in terms of the increased electron-rich character decreasing the magnitude of k_{-1} or increasing the magnitude of at least one of k_2–k_4. In fact, the two effects may be viewed as synergistic. Specifically, the electron-donating methoxy groups will stabilize the one-electron oxidized form of the β-diketonate with respect to reduction, decreasing k_{-1}, and the increased electron density should facilitate oxidation, thereby increasing k_2.

The observed lack of reactivity for the unsubstituted Ni^{II} β-diketonate complexes **7–9** was investigated by using a crossover-type experiment. Specifically, an acetonitrile solution containing equimolar amounts of methoxy-substituted **7** and the sodium salt of dibenzoylmethane was irradiated for 20 h, after which time the reaction was evaluated by using ^1H NMR spectroscopy under paramagnetic conditions. At this point, a mixture of **7** and **9** was present. In the absence of irradiation, formation of a similar mixture took > 7 days to form. These combined results indicate that in a similar manner to **4–6**, the unsubstituted complexes **7–9** undergo a photochemical reaction that labilizes the β-diketonate ligand. The lack of formation of oxidation, α-cleavage, or flavone products in these systems appears to be due to the lack of the reactive 2-chloro moiety in the labilized β-diketonate radical species. The chloro substituent may be necessary as a leaving group[26] to enable the formation of a vicinal triketone, or to enhance the electrophilic character of the α-carbon center.

Conclusion

Oxidative carbon–carbon bond-cleavage reactions of relevance to biological processes are of current interest, including those involving aliphatic carbon–carbon bond cleavage in β-diketone substrates. Herein, we demonstrate that this type of oxidative chemistry can be achieved through photochemical reduction of Ni^{II} 2-chloro-1,3-diketonate complexes under aerobic conditions. We propose that the reduced nickel center generated in these reactions activates dioxygen to form superoxide and initiate a reaction sequence that ultimately results in the formation of carboxylic acid products. This novel reactivity has relevance to that proposed for the iron-containing Dke1 enzyme in which the metal center mediates electron transfer from the β-diketonate ligand to O_2, leading to the formation of superoxide. Overall, this work outlines a new approach toward examining chemistry of relevance to metal-containing dioxygenase enzymes that cleave a β-diketone ligand.

Experimental Section

General methods: All reagents and solvents were obtained from commercial sources, and were used without further purification unless otherwise

noted. The 6-Ph_2TPA ligand (*N*,*N*-bis-[(6-phenyl-2-pyridyl)methyl]-*N*-[(2-pyridyl)methyl]amine), 1,3-di(4-tolyl)propane-1,3-dione (**2b**), [(6-Ph_2TPA)Ni{PhC(O)CHC(O)Ph}][ClO_4] (**9**), [(6-Ph_2TPA)Ni(Cl)-(CH_3CN)][ClO_4] (**10**), [(6-Ph_2TPA)Ni(CH_3CN)$_2$][ClO_4]$_2$ (**13**) were synthesized according to literature procedures.[7,17,21,27] 1,3-Di(4-methoxyphenyl)propane-1,3-dione and 1,3-diphenylpropane-1,3-dione were purchased from TCI and ACROS, respectively, and were used as received. Dry acetonitrile was prepared according to a literature procedure[28] and was used in the metal complex syntheses.

Physical methods: ^{1}H NMR spectra of organic compounds were obtained by using a JEOL ECX-300 or Bruker ARX-400 NMR spectrometer. Chemical shifts were referenced to the residual solvent peak in CD_2HCN ($\delta = 1.94$ ppm, quintet). ^{1}H NMR spectra of paramagnetic Ni^{II} complexes were obtained by using a Bruker ARX-400 spectrometer and parameters as previously described.[17] FT-IR data were collected on a Shimadzu FTIR-8400 spectrometer as KBr pellets. UV/Vis data was collected on a HP8453A spectrometer at ambient temperature. Photoreactions were carried out in a Srinivasan–Griffin Rayonet photochemical reactor equipped with 8 RPR-3500 lamps, having $\lambda_{max} = 350$ nm. GC-MS data was obtained with a Shimadzu GCMS-QP5000 gas chromatograph/mass spectrometer with a GC-17A gas chromatograph, by using an Alltech EC-5 30 mm × 0.25 mm × 0.25 μm thin film capillary column and temperature program: $T_{Initial}$: 30 °C (3 min); temperature gradient: 23 °C min^{-1}; T_{Final}: 250 °C (10 min). Quantum yields were determined by ferrioxalate actinometry, by using an integrative analysis method.[29] Anaerobic electrochemical measurements were carried out in a drybox under a N_2 atmosphere in CH_3CN with [Bu_4N][ClO_4] (0.1 M) as the supporting electrolyte by using a model ED401 computer-controlled potentiostat (eDAQ). A three-electrode configuration with a glassy carbon working electrode, a Ag wire quasi-reference electrode with an Fc/Fc^+ internal reference, and a platinum wire auxiliary electrode was used. Aerobic electrochemical studies were performed after purging the cell with O_2. The potential values were referenced to an internal ferrocenium/ferrocene couple, which is reported to be +0.38 V versus a saturated calomel electrode (SCE) with [NBu_4][ClO_4] in CH_3CN.[30]

Preparation of 2-chloro-1,3-di(4-methoxyphenyl)propane-1,3-dione (3a): A solution comprised of acetonitrile (20 mL), aqueous NH_4Cl (1.0 M, 20 mL), and aqueous $RuCl_3$ (0.10 M, 250 μL) was cooled in an ice-bath. Oxone (4.08 g, 6.64 mmol) was added to this solution, which resulted in the formation of a yellow suspension. The mixture was then warmed to room temperature. Dropwise addition of a solution of 1,3-di(4-methoxyphenyl)propane-1,3-dione (0.382 g, 1.34 mmol) in ethyl acetate (10 mL) resulted in darkening to a purplish color. After stirring overnight at ambient temperature, the solution was again a yellow color. The suspension was then diluted with water (100 mL) and the mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, filtered, and the filtrate was brought to dryness under reduced pressure. The pale yellow solid was recrystallized from hot ethanol to give pale yellow crystals (338 mg, 79 %). M.p. 94–96 °C; ^{1}H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 7.96$ (d, ^3J(H,H) = 8.9 Hz, 4H; Ar-H), 7.03 (d, ^3J(H,H) = 8.9 Hz, 4H; Ar-H), 6.83 (s, 1H; CH), 3.87 ppm (s, 6H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 25 °C): $\delta = 189.8$ (C=O), 166.0 (C_q^{Ar}), 132.8 (CH^{Ar}), 128.1 (C_q^{Ar}), 115.7 (CH^{Ar}), 62.8 (CHCl), 56.9 ppm (CH_3); IR (KBr): $\tilde{\nu} = 1687$ (C=O), 1659, 1601, 1572 cm^{-1}; GC-MS: *m/z* (%): 320 (0.38), 318 (0.18).

Preparation of 2-chloro-1,3-bis(4-methylphenyl)propane-1,3-dione (3b): Compound **3b** (32 %) was prepared in a similar manner to **3a**. M.p. 140–141 °C; ^{1}H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 7.87$ (d, ^3J(H,H) = 8.5 Hz, 4H; Ar-H), 7.35 (d, ^3J(H,H) = 8.5 Hz, 4H; Ar-H), 6.89 (s, 1H; CH), 2.45 ppm (s, 6H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 25 °C): $\delta =$ 191.0 (C=O), 147.3 (C_q^{Ar}), 132.8 (C_q^{Ar}), 131.1 (CH^{Ar}), 130.4 (CH^{Ar}), 62.7 (CHCl), 22.1 ppm (CH_3); IR (KBr): $\tilde{\nu} = 1695$ (C=O), 1674, 1604 cm^{-1}; GC-MS: *m/z* (%): 286 (1.1), 288 (0.4); elemental analysis calcd (%) for $C_{17}H_{15}ClO_2 \cdot 0.2H_2O$: C 70.31, H 5.35; found: C 70.50, H 5.31.

Preparation of 2-chloro-1,3-bisphenylpropane-1,3-dione (3c): Compound **3c** (83 %) was prepared in a similar manner to **3a**. M.p. 71–72 °C; ^{1}H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 7.98$ (d, ^3J(H,H) = 7.2 Hz, 4H; Ar-H), 7.69 (t, ^3J(H,H) = 8.4 Hz, 2H; Ar-H), 7.55 (t, ^3J(H,H) = 6.7 Hz, 4H; Ar-H), 6.97 ppm (s, 1H; CH); IR (KBr): $\tilde{\nu} = 1699$ (C=O), 1680, 1595, 1580 cm^{-1}; GC-MS: *m/z* (%): 258 (1.5), 260 (0.5).

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.[31]

Preparation of [(6-Ph_2TPA)Ni{(4-OCH_3Ph)C(O)C(Cl)C(O)(4-OCH_3Ph)}][ClO_4] (4): $Ni(ClO_4)_2 \cdot 6H_2O$ (29 mg, 79 μmol) was dissolved in dry acetonitrile (2 mL), and this solution was added to solid 6-Ph_2TPA (35 mg, 79 μmol). The resulting solution was stirred for 15 min, during which time it became purple. This solution was added to solid 2-chloro-1,3-di(4-methoxyphenyl)propane-1,3-dione (25 mg, 79 μmol) and the resulting mixture was stirred until everything had dissolved. The pale-purple solution was then added to solid $Me_4NOH \cdot 5H_2O$ (13 mg, 79 μmol) and the mixture was stirred overnight at ambient temperature, during which time it became yellow. The solvent was removed from the reaction mixture under vacuum, the remaining solid was redissolved in CH_2Cl_2, and the solution was filtered through a glass wool/celite plug. Concentration of the filtrate under vacuum, followed by the addition of an excess of hexanes resulted in the deposition of a yellow solid (50 mg, 70 %) that was dried under vacuum. IR (KBr): $\tilde{\nu} = 1603$, 1346, 1094 (ClO_4), 623 cm^{-1} (ClO_4); HRMS (ESI): *m/z* calcd for $C_{47}H_{40}N_4ClO_4Ni^+$: 817.209 [$M-ClO_4$]$^+$; found: 817.209; elemental analysis calcd (%) for $C_{47}H_{40}N_4Cl_2O_8Ni$: C 61.45, H 4.39, N 6.10; found: C 61.48, H 4.90, N 5.99.

Preparation of [(6-Ph_2TPA)Ni{(4-CH_3Ph)C(O)C(Cl)C(O)(4-CH_sPh)}][ClO_4] (5): Compound **5** (62 %) was prepared and crystallized in a manner similar to that described for **4** by using the appropriate starting materials. IR (KBr): $\tilde{\nu} = 1346$, 1094 (ClO_4), 623 cm^{-1} (ClO_4); HRMS (ESI): *m/z* calcd for $C_{47}H_{40}N_4ClO_2Ni^+$: 785.219 [$M-ClO_4$]$^+$; found: 785.219; elemental analysis calcd (%) for $C_{47}H_{40}N_4Cl_2O_6Ni \cdot 1.5CH_2Cl_2$: C 57.46, H 4.27, N 5.53; found: C 57.19, H 4.26, N 5.50.

Preparation of [(6-Ph_2TPA)Ni{PhC(O)C(Cl)C(O)Ph}][ClO_4] (6): Compound **6** (83 %) was prepared and crystallized in a manner similar to that described for **4** by using the appropriate starting materials. IR (KBr): $\tilde{\nu} =$ 1352, 1096 (ClO_4), 623 cm^{-1} (ClO_4); HRMS (ESI): *m/z* calcd for $C_{45}H_{36}N_4ClO_2Ni^+$: 757.188 [$M-ClO_4$]$^+$; found: 757.189; elemental analysis calcd (%) for $C_{45}H_{36}N_4Cl_2O_6Ni$: C 62.95, H 4.23, N 6.53; found: C 63.22, H 4.18, N 6.65.

Preparation of [(6-Ph_2TPA)Ni{(4-OCH_3Ph)C(O)CHC(O)(4-OCH_3Ph)}][ClO_4] (7): Compound **7** (80 %) was prepared and crystallized in a manner similar to that described for **4** by using the appropriate starting materials. IR (KBr): $\tilde{\nu} = 1094$ (ClO_4), 623 cm^{-1} (ClO_4); elemental analysis calcd (%) for $C_{47}H_{41}N_4ClO_8Ni \cdot 0.2(CH_2Cl_2)$: C 62.90, H 4.63, N 6.22; found: C 62.84, H 4.65, N 6.18.

Preparation of [(6-Ph_2TPA)Ni{(4-CH_3Ph)C(O)CHC(O)(4-CH_3Ph)}][ClO_4] (8): Compound **8** (80 %) was prepared and crystallized in a manner similar to that described for **4** by using the appropriate starting materials. IR (KBr): $\tilde{\nu} = 1094$ (ClO_4), 623 cm^{-1} (ClO_4); elemental analysis calcd (%) for $C_{47}H_{41}N_4ClO_6Ni$: C 66.67, H 5.14, N 6.42; found: C 66.80, H 5.50, N 6.48.

Preparation of [(6-Ph_2TPA)Ni{O_2C(4-OCH_3Ph)}][ClO_4] (11): Solid $Ni(ClO_4)_2 \cdot 6H_2O$ (22 mg, 61 μmol) was dissolved in acetonitrile, and this solution was added to 6-Ph_2TPA (27 mg, 61 μmol). The resulting mixture was stirred for one hour to form a homogeneous purple solution. Anisic acid (9.3 mg, 61 μmol) was dissolved in methanol (1 mL) and this solution was added to the solution of the Ni^{II} complex. The resulting mixture was stirred for 15 min and then added to solid $Me_4NOH \cdot 5H_2O$ (11 mg, 61 μmol). The mixture was stirred overnight during which time a blue/green solution formed. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. This solution was passed through a glass wool/celite plug twice and then the filtrate was reduced in volume under reduced pressure. The final product was precipitated by the addition of an excess of hexanes and was dried under vacuum (26 mg, 47 %). IR (KBr): $\tilde{\nu} = 1607$, 1096 (ClO_4), 623 cm^{-1} (ClO_4); HRMS (ESI): *m/z* calcd for $C_{38}H_{33}ClN_4NiO_7^+$: 651.1906 [$M-ClO_4$]$^+$; found: 651.1913; elemental analysis calcd (%) for $C_{38}H_{33}ClN_4NiO_7 \cdot 0.2C_6H_{14}$: C 61.83, H 4.76, N 7.25; found: C 61.73, H 4.62, N 7.66.

Preparation of [(6-Ph_2TPA)Ni{O_2C(4-OCH_3Ph)}$_2$] (12): Solid $Ni(ClO_4)_2$·6H_2O (30 mg, 81 μmol) dissolved in acetonitrile (1 mL) was added to 6-Ph_2TPA (40 mg, 80 μmol) and the resulting solution was stirred for one hour during which time it became pale purple. Anisic acid (25 mg, 162 μmol) was dissolved in acetonitrile (1 mL) and this solution was added to solid Me_4NOH·5H_2O (29 mg, 162 μmol). The resulting mixture was stirred for 1 h during which time the solution became yellow. The Ni^{II}-containing solution was combined with the anisic acid/Me_4NOH·5H_2O solution and the mixture was stirred overnight, forming a blue/green homogeneous solution. The solvent was then removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 and filtered through a glass wool/celite plug. The filtrate was brought to approximately 1 mL in volume under reduced pressure and the final product was precipitated by the addition of hexanes (41 mg, 63%). IR (KBr): $\tilde{\nu}$ = 1605 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{38}H_{33}ClN_4NiO_7^+$: 651.1906 $[M-CH_3OC_6H_4CO_2]^+$; found: 651.1918; elemental analysis calcd (%) for $C_{46}H_{40}N_4O_6Ni$·1.5H_2O: C 66.51, H 5.22, N 6.75; found: C 66.72, H 5.18, N 6.81.

Product recovery for photochemical reactions: To identify products of the photo-reactions, solutions of complexes **4**–**6** in acetonitrile (5.0 mL, 2.0 mM) were irradiated for 20 h. The solvent was then removed under reduced pressure and the crude reaction mixtures were analyzed by ^{1}H NMR spectroscopy by using paramagnetic parameters. To extract the organic component, each crude reaction mixture was passed through a short silica column, eluting with ethyl acetate, providing yields greater than 80% (≈2.5 mg) of the expected mass of the β-diketonate in the starting compound. The inorganic fraction was also recovered by eluting with acetonitrile, followed by methanol. The organic fraction was then analyzed by ^{1}H NMR spectroscopy and GC-MS and the inorganic fraction by ^{1}H NMR spectroscopy by using paramagnetic parameters. As a control reaction, complex **4** (0.01 mmol) was passed through a short silica column by using the same solvents, and dissociation of the complex to form the 2-chloro-1,3-dione (**3a**, 85% recovery) and [(6-Ph_2TPA)Ni-$(CH_3CN)_2$][ClO_4]$_2$ (**13**) was observed.

Reactivity studies: For UV/Vis experiments, solutions of the complexes **4**–**6** in acetonitrile (0.04 mM) were prepared. These solutions were found to be stable in the absence of light under aerobic and anaerobic conditions. Aliquots of these solutions (3.0 mL) were placed in a UV/Vis cell. The cell was then irradiated at 350 nm, monitoring the reaction by UV/Vis spectroscopy. For anaerobic reactions, the solutions were prepared in a vacuum atmosphere glovebox under an atmosphere of N_2, and the UV/Vis cell was sealed with a Teflon stopcock. For reactions that included dihydroanthracene, solutions were prepared as described above with the addition of dihydroanthracene (2.0 mM).

Reactivity of 4–6 with KO_2: Solutions of **4**–**6** in acetonitrile (4.0 mL, 2.0 mM) were treated with KO_2 (1.0 mg, 0.014 mmol) in the presence of 18-crown-6 (3.7 mg, 0.014 mmol) and stirred for 15 min. The color of the solution rapidly faded from yellow to colorless. The solvent was then removed under reduced pressure, and the organic components of the reactions separated by use of a silica column and analyzed by GC-MS, similar to the photochemical reactions. In all cases, the major organic product, as determined by GC-MS, was the corresponding benzoic acid derivative **I**.

X-ray crystallography: Single crystal samples of **5**, **6**, and **8** were mounted on a glass fiber by using a viscous oil and then transferred to a Nonius KappaCCD diffractometer ($Mo_{K\alpha}$, λ = 0.71073 Å) for data collection at 150(1) K. Methods for determination of cell constants and unit cell refinement have been previously reported.[32] Each structure was solved by using a combination of direct methods and heavy atom methods by using SIR97. All non-hydrogen atoms were refined with anisotropic displacement coefficients.

Complexes **5**, **6** and **8** crystallize in the triclinic crystal system in the space group $P\bar{1}$. All hydrogen atoms in these complexes were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl})$ and their coordinates were allowed to ride on their respective carbon by using SHELXL97. For **5** and **6**, $Z = 2$, whereas for **8**, $Z = 4$ and two independent molecules are present in the asymmetric unit. For **5**, three atoms of the perchlorate anion were found to be disorderd over two positions (0.68:0.32). One disordered molecule of Et_2O is present per formula unit in the structure of **5**. In the structure of **6**, two oxygen atoms of the perchlorate anion are disorded over two positions (0.86:0.14). For **8**, there are two molecules of CH_2Cl_2 per formula unit. CCDC-827741 (**5**·$C_4H_{10}O$), CCDC-827742 (**6**), and CCDC-827743 (**8**·2CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] G. Grogan, *Biochem. J.* **2005**, *388*, 721–730.
[2] T. Pochapsky in *Metal Ions in Life Sciences, Vol. 2, Nickel and Its Suprising Impact in Nature* (Eds.: A. Sigel, H. Sigel, R. K. O. Sigel), Wiley, New York, **2007**, pp. 473–500.
[3] G. D. Straganz, B. Nidetzky, *J. Am. Chem. Soc.* **2005**, *127*, 12306–12314.
[4] S. Leitgeb, G. D. Straganz, B. Nidetzky, *Biochem. J.* **2009**, *418*, 403–411.
[5] I. Siewert, C. Limberg, *Angew. Chem.* **2008**, *120*, 8071–8074; *Angew. Chem. Int. Ed.* **2008**, *47*, 7953–7956.
[6] M. G. M. B. Martin, M. Hörner, M. B. Behm, F. S. Nunes, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1229–1233.
[7] E. Szajna-Fuller, K. Rudzka, A. M. Arif, L. M. Berreau, *Inorg. Chem.* **2007**, *46*, 5499–5507.
[8] L. M. Berreau, T. Borowski, K. Grubel, C. J. Allpress, J. P. Wickstrom, M. E. Germain, E. V. Rybak-Akimova, D. L. Tierney, *Inorg. Chem.* **2011**, *50*, 1047–1057.
[9] a) Y. L. Chow, H. Li, M. S. Yang, *J. Chem. Soc. Perkin Trans. 2* **1990**, 17–24; b) Y. L. Chow, H. Li, *Can. J. Chem.* **1986**, *64*, 2229–2231; c) Y. L. Chow, G. E. Buono-Core, *J. Chem. Soc. Chem. Commun.* **1985**, 592–594.
[10] a) M. T. Kieber-Emmons, C. G. Riordan, *Acc. Chem. Res.* **2007**, *40*, 618–625; b) A. Company, S. Yao, K. Ray, M. Driess, *Chem. Eur. J.* **2010**, *16*, 9669–9675.
[11] R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed., Wiley, New York, **1999**, p. 715.
[12] A. Podgorsek, M. Jurisch, S. Stavber, M. Zupan, J. Iskra, J. A. Gladysz, *J. Org. Chem.* **2009**, *74*, 3133–3140.
[13] H. M. Meshram, P. N. Reddy, P. Vishnu, K. Sadashiv, J. S. Yadav, *Tetrahedron Lett.* **2006**, *47*, 991–995.
[14] G. I. Roshchupkina, Y. V. Gatilov, T. V. Rybalova, V. A. Reznikov, *Eur. J. Org. Chem.* **2004**, 1765–1773.
[15] a) J. C. Taylor, A. B. McLaren, *J. Chem. Soc. Dalton Trans.* **1979**, 460–464; b) V. G. Isakova, I. A. Baidina, N. B. Morozova, I. K. Igumenov, *Polyhedron* **2000**, *19*, 1097–1103; c) D. C. Ware, W. R. Wilson, W. A. Denny, C. E. F. Rickard, *J. Chem. Soc. Chem. Commun.* **1991**, 1171–1173; d) C. A. Vock, A. K. Renfrew, R. Scopelliti, L. Juillerat-Jeanneret, P. J. Dyson, *Eur. J. Inorg. Chem.* **2008**, 1661–1671; e) E. D. Estes, R. P. Scaringe, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1976**, *15*, 1179–1182; f) C. A. Kavounis, L. C. Tzavellas, C. J. Cardin, Y. Zubavichus, *Struct. Chem.* **1999**, *10*, 411; g) S. Sans-Lenain, A. Gleizes, *Inorg. Chim. Acta* **1993**, *211*, 67–75; h) V. V. Sharutin, O. K. Sharutina, O. P. Zadachina, A. N. Zakharova, V. A. Reutov, N. P. Shapkin, V. K. Bel'skii, *Zh. Obshch. Khim.* **2000**, *70*, 1573–1575.
[16] E. Szajna, A. M. Arif, L. M. Berreau, *J. Am. Chem. Soc.* **2005**, *127*, 17186–17187.

[17] E. Szajna, P. Dobrowolski, A. L. Fuller, A. M. Arif, L. M. Berreau, *Inorg. Chem.* **2004**, *43*, 3988–3997.
[18] B. Košmrlj, B. Sket, *Org. Lett.* **2007**, *9*, 3993–3996.
[19] R. L. Lintvedt, H. D. Gafney, *J. Am. Chem. Soc.* **1970**, *92*, 6996–6997.
[20] F. D. Lewis, A. M. Miller, G. D. Salvi, *Inorg. Chem.* **1995**, *34*, 3173–3181.
[21] P. S. Singh, D. H. Evans, *J. Phys. Chem. B.* **2006**, *110*, 637–644.
[22] N. Tada, M. Shomura, H. Nakayama, T. Miura, A. Itoh, *Synlett* **2010**, 1979–1983.
[23] We could not conclusively identify the formation of the benzil analogue 4,4′-dimethoxybenzil in the product mixture genenerated from the reactions of **4**. This may be influenced by the presence of the methoxy substitutent, as the propensity of the triketone to undergo migration reactivity leading to benzil formation will be influenced by the relative electrophilicity of carbonyl centers. V. H. Lé Dao, F. Dayer, L. Duc, H. Rodé-Gowal, H. Dahn, *Helv. Chim. Acta* **1974**, *57*, 2215–2223.
[24] a) L. Shu, Y. Shi, *Tetrahedron* **2001**, *57*, 5213–5218; b) N. A. Porter, H. Yin, D. A. Pratt, *J. Am. Chem. Soc.* **2000**, *122*, 11272–11273.
[25] K. Nakatani, J. Shirai, R. Tamaki, I. Saito, *Tetrahedron Lett.* **1995**, *36*, 5363–5366.
[26] S. J. Coats, H. H. Wasserman, *Tetrahedron Lett.* **1995**, *36*, 7735–7738.
[27] P. K. Dhondi, P. Carberry, J. D. Chisholm, *Tetrahedron Lett.* **2007**, *48*, 8743–8746.
[28] W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth–Heinemann, Boston, **1996**.
[29] H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem.* **2004**, *76*, 2105–2146.
[30] W. Connelly, W. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.
[31] W. C. Wolsey, *J. Chem. Educ.* **1973**, *50*, A335.
[32] E. Szajna, M. M. Makowska-Grzyska, C. C. Wasden, A. M. Arif, L. M. Berreau, *Inorg. Chem.* **2005**, *44*, 7595–7605.

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