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by $^{31}P\{^1H\}$ NOESY is ascribed to the relatively slow interconversion between the covalent and dative Ni–Pd-bonded isomers of **1**.

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(13) (a) Reinking, M. K.; Kullberg, M. L.; Cutler, A. R.; Kubiak, C. P. *J. Am. Chem. Soc.* **1985**, *107*, 3517. (b) Kullberg, M. L.; Lemke, F. R.; Powell, D. R.; Kubiak, C. P. *Inorg. Chem.* **1985**, *24*, 3589.

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IR Evidence for the Formation of an η^2(C,O)-α-Ketoacyl Complex upon Low-Temperature Photolysis of (η-C_5H_4Me)(CO)(NO)Mn–C{O}C{O}Tol

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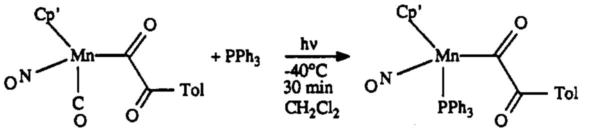
A surprising feature of the chemistry of the α-ketoacyl complex Cp′(CO)(NO)Mn-C{O}C{O}Tol (**1**) (Cp′ = η-C_5H_4Me) is its resistance to CO deinsertion to form an acyl complex when either heated or irradiated.[1] Photolysis of **1**, for example, in the presence of PPh_3 did not lead to deinsertion but instead gave clean photosubstitution of PPh_3 (eq 1).[1] It was thought that this result might be due to the formation of an intermediate with an α-ketoacyl ligand coordinated in an η^2(C,O) fashion that stabilizes the coordinatively unsaturated complex resulting from photoinduced CO loss. To address this question, a detailed low-temperature photochemical study of **1** was undertaken, and those results are reported herein.

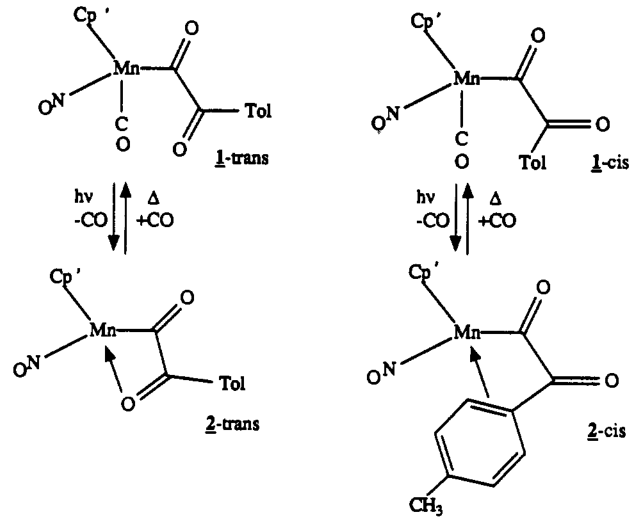


(1)

Experimental Section

Complex **1** was prepared as described in ref 1. Solvents used were dried by distillation from $CaCl_2$ (CH_2Cl_2) or Na (2-MeTHF). IR spectra were recorded on a Nicolet 7199B FTIR spectrometer using a liquid-nitrogen-cooled MCT detector (32 scans, resolution 1.0 cm^{-1}). For the low-temperature measurements, use was made of an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat. All photochemical experiments were conducted by using the 436-nm line of an Osram HBO 200W/2 200-W Hg lamp.

Scheme I



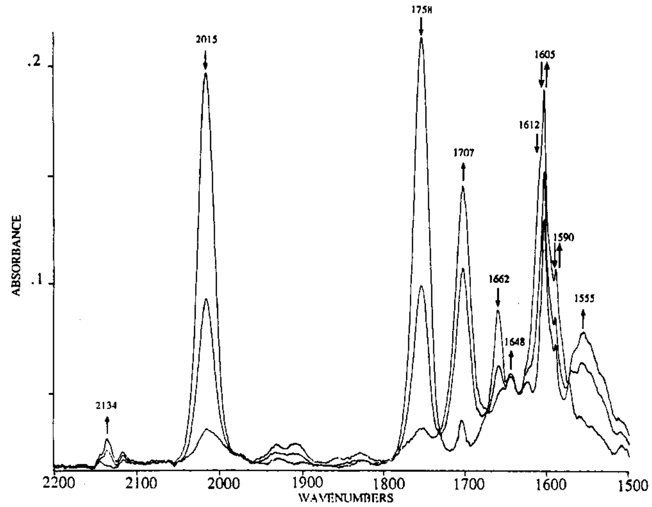


Figure 1. IR spectral changes occurring upon 436-nm irradiation of complex **1** in CH_2Cl_2 at −100 °C.

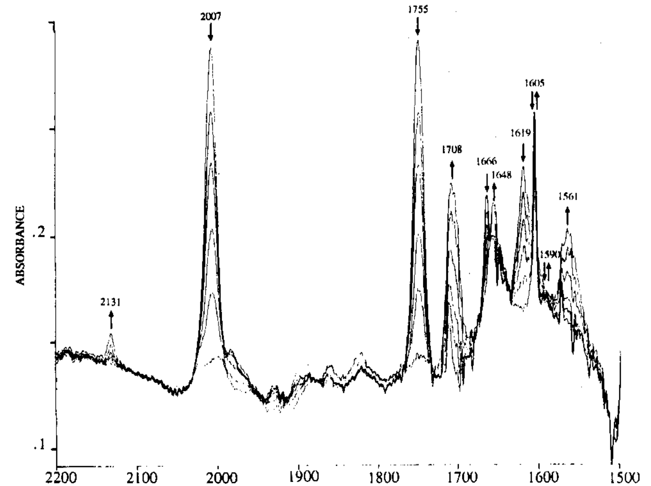


Figure 2. IR spectral changes occurring upon 436-nm irradiation of complex **1** in 2-MeTHF at −140 °C.

Results

Complex **1** was studied at −140 °C in 2-MeTHF and at −100 °C in CH_2Cl_2, conditions under which both s-cis (**1**-cis) and s-trans (**1**-trans) isomers of the α-ketoacyl ligand are present (see Scheme I). Table I lists the IR bands observed for these isomers and their assignments. Like the previously studied palladium α-ketoacyl

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(1) Sheridan, J. B.; Johnson, J. R.; Handwerker, B. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2404.

Table I. IR Bands and Their Assignments for Complex **1** and Its Photoproduct (**2**)[a]

complex	solvent	temp, °C	$\nu(C{\equiv}O)$	$\nu(NO)$	$\nu(C{=}O)^{\alpha}_{cis}$	$\nu(C{=}O)^{\beta}_{cis}$	$\nu(C{=}O)^{\alpha}_{trans}$	$\nu(C{=}O)^{\beta}_{trans}$
1	2-MeTHF	-140	2007	1755	1590	1666	1605	1619
1	CH_2Cl_2	-100	2015	1758	1590	1662	1605	1612
2	2-MeTHF	-140		1708	1590	1648	1605	1561
2	CH_2Cl_2	-100		1707	1590	1648	1605	1555

[a] Values in cm^{-1}.

complexes,[2] the s-cis isomer is presumed to have the larger energy separation between the bands assigned to the α-carbonyl ($\nu(C{=}O)^{\alpha}$) and β-carbonyl ($\nu(C{=}O)^{\beta}$) groups of the ligand, with the lower energy band in each isomer assigned to the α-carbonyl. Figures 1 and 2 present the IR spectral changes accompanying the photoreaction of **1** in CH_2Cl_2 at -100 °C and in 2-MeTHF at -140 °C, respectively.

Discussion

Irradiation of complex **1** with the 436-nm line of a medium-pressure mercury lamp induced loss of the CO ligand as evidenced by the disappearance of the metal carbonyl band at 2007/2015 cm^{-1} and the growth of the IR band of free CO (2134 cm^{-1} in CH_2Cl_2, 2131 cm^{-1} in 2-MeTHF). The nitrosyl band $\nu(NO)$ shifted to lower frequency with the same value observed for both isomers. It is noteworthy that the IR bands assigned to the α-carbonyl groups of the α-ketoacyl ligand in both the s-cis and s-trans isomers do not shift during the reaction whereas the bands due to the β-carbonyl groups are very sensitive to the loss of CO, especially that of the s-trans isomer. Its frequency shifts by more than 50 cm^{-1} to lower energy whereas $\nu(C{=}O)^{\beta}_{cis}$ only shifts by ~15 cm^{-1}. Upon warming of the irradiated solutions, back-reaction occurred beginning at ~-100 °C to re-form the original isomers of the α-ketoacyl complex **1**, but the spectra did not permit a determination of which isomer reacted faster.

The interpretation of these results is straightforward. The frequency lowering of $\nu(NO)$ is caused by the increase of π-back-bonding after loss of CO. The open site created by this reaction is apparently not occupied by a solvent molecule, since the IR bands of the photoproduct hardly differ in CH_2Cl_2 and 2-MeTHF. The latter is known to be a good coordinating solvent at -140 °C.[3] It is therefore proposed that in both isomers this open site is occupied by some part of the α-ketoacyl ligand. The lack of an observed shift in the IR bands assigned to the α-carbonyl groups of the two isomers indicates that these groups do not occupy the coordination site. For the s-trans isomer, the β-carbonyl of the α-ketoacyl ligand is favorably oriented for coordination of the carbonyl oxygen (Scheme I) and such coordination is indicated by the large photoinduced shift of the IR band assigned to the β-carbonyl of this isomer. For the s-cis isomer, we suggest that the coordination site opened by photoejection of CO is either weakly coordinated by the tolyl group, as indicated in Scheme I, or is unoccupied.

The low-temperature photolysis results presented above are consistent with the observation that room-temperature photolysis of complex **1** in the presence of PPh_3 does not lead to CO deinsertion but rather to clean photosubstitution of PPh_3 for CO (eq 1). The above results suggest that intermediates like those shown in Scheme I may be produced in the latter photosubstitution reaction and may thus stabilize the "open" coordination site until PPh_3 displaces the coordinated α-ketoacyl ligand in an S_N2-type reaction.

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(2) (a) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166. (b) Chen, J.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 148. (c) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683. (d) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 692. (e) Fayos, J.; Dobrzynski, E.; Angelici, R. J.; Clardy, J. *J. Organomet. Chem.* **1973**, *59*, C33. (f) Bochmann, M.; Hawkins, L.; Hursthouse, M. B.; Short, R. L. *J. Organomet. Chem.* **1987**, *332*, 361. (g) des Abbayes, H. *New J. Chem.* **1987**, *11*, 535.

(3) See, for example: van Dijk, H. K.; Stufkens, D. J.; Oskam, A.; Rotteveel, M.; Heijdenrijk, D. *Organometallics* **1987**, *6*, 1665.

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Conversion of $[ReH(acac)_2(PPh_3)_2]PF_6$ to *cis*-$[Re(acac)_2(PPh_3)_2]PF_6$ through a Coupled Oxidation/Deprotonation Reaction

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Introduction

In the course of a recent study in which we examined the reactivity of $ReH_7(PPh_3)_2$ toward various donor ligands, we reported the syntheses and structures of the Re(IV)–Re(III) redox pair $[ReH(acac)_2(PPh_3)_2]PF_6$ and $ReH(acac)_2(PPh_3)_2$, where acac is the anion of 2,4-pentanedione.[1] The Re(IV) salt $[ReH(acac)_2(PPh_3)_2]PF_6$ is obtained by a simple one-electron oxidation of the neutral Re(III) complex $ReH(acac)_2(PPh_3)_2$. When further oxidation of the Re(IV) complex was attempted, a monohydride Re(V) complex was not formed; instead, a new Re(III) cation was produced through the deprotonation of the unstable species $[ReH(acac)_2(PPh_3)_2]^{2+}$. In this report, we describe the formation of *cis*-$[Re(acac)_2(PPh_3)_2]PF_6$ (**1**) from the reaction of $[ReH(acac)_2(PPh_3)_2]PF_6$ with the oxidant $NOPF_6$. The crystal structure of **1** is also reported, thereby permitting a structural comparison to the previously reported structures of the precursor complexes, $[ReH(acac)_2(PPh_3)_2]PF_6$ and $ReH(acac)_2(PPh_3)_2$, as well as to other six-coordinate, mononuclear acetylacetonate complexes of rhenium.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry nitrogen. All solvents were thoroughly deoxygenated prior to use. The compounds $ReH(acac)_2(PPh_3)_2$ and $[ReH(acac)_2(PPh_3)_2]PF_6$ were prepared by methods described elsewhere.[1] Both $NOPF_6$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were obtained from commercial sources. All reagents and solvents were obtained from commercial sources.

Infrared spectra were recorded in the range 4000–450 cm^{-1} as Nujol mulls between KBr plates on a Perkin Elmer Model 1800 IR Fourier transform spectrometer. Electronic absorption spectra were recorded in the range 900–300 nm on an IBM Instruments 9420 UV-visible spectrophotometer. Cyclic voltammetric measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions the ferrocenium/ferrocene couple is at $E_{1/2}$ = +0.47 V vs Ag/AgCl. Bulk electrolyses

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(1) Fanwick, P. E.; Leeaphon, M.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 676.