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Low temperature matrix photochemistry of $M_2(CO)_4(\mu$ -S-*t*-Bu)₂ and $[M(CO)_2Cl_2]^{1-}$ anions, where M = Rh and Ir

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Abstract

Photolysis of $M_2(CO)_4(\mu$ -S-*t*-Bu)₂, where M = Rh or Ir, in Nujol matrices at ca. 90 K results in simple CO loss to form a tricarbonyl intermediate analogous to that observed for Rh₂(CO)₄(μ -Cl)₂. Photolysis of the anions, [M(CO)₂Cl₂]¹⁻, where M = Rh or Ir, in inert ionic matrices at ca. 90 K, results in CO-loss to form an intermediate analogous to that formed by Rh(CO)₂(*i*-Pr₂HN)Cl. Finally, photolysis of *trans*-Ir(CO)(PMe₃)₂Cl in a Nujol matrix at ca. 90 K gives rise to a new species whose carbonyl band is shifted slightly down in energy as has been observed for *trans*-Rh(CO)(PMe₃)₂Cl. In all cases the iridium compounds behave similarly to the rhodium species although the photon energy for iridium photochemistry is typically above that of the rhodium compounds. © 2004 Elsevier B.V. All rights reserved.

Keywords: Rhodium photochemistry; Iridium photochemistry matrix photochemistry; Ionic matrix

1. Introduction

Some years ago Bitterwolf and coworkers [1] reported the photochemistry of $Rh_2(CO)_4(\mu$ -Cl)₂ in both inert gas matrices and frozen Nujol matrices. Under these conditions clean loss of CO was observed to yield a tricarbonyl intermediate that was fully characterized by IR. Somewhat more recently we have reported the photochemistry of *cis*-Rh(CO)₂(ammine)Cl derivatives in frozen Nujol and established the presence of two isomeric CO-loss intermediates in which the remaining CO is either *trans* to Cl or the ammine ligand [2]. Our continued interest in the application of rhodium derivatives in photocatalytic reactions prompted us to reopen these investigations to thiolato bridged rhodium and iridium derivatives in which the thiol bridge is unusually stable, as well as the catalytically underutilized [M(CO)₂Cl₂]^{1–} anions. Relevant to these investigations we have also expanded our earlier studies on trans-Rh(CO)(PMe₃)₂Cl with the photolysis of trans-Ir(CO)(PMe₃)₂Cl. This paper describes the examination of these compounds in frozen Nujol, or, in the case of the carbonyl chloride anions, inert ionic matrices.

2. Experimental

Rh₂(CO)₄(μ -S-*t*-Bu)₂ [10], [NBu₄][Rh(CO)₂Cl₂] [19], [NMe₄][Ir(CO)₂Cl₂] [20], and Ir(CO)(PMe₃)₂Cl [21] were prepared by literature procedures. Ir₂(CO)₄(μ -S-*t*-Bu)₂ was prepared by reaction of LiS-*t*-Bu with [NMe₄][Ir-(CO)₂Cl₂] in THF by analogy to reactions of [Rh(CO)₂Cl₂]^{1–} reported by Klack [22]. The product from this reaction was identical with that reported by deMontavzon and Poilblanc [23]. NEt₃Oct PF₆ and bmim PF₆ are dried before use by heating to ca. 90° C under vacuum for several days.

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Photochemical methods have been described elsewhere [1]. Preparation of samples in NEt₃Oct PF₆ require first through mixing of the solids in an approximate 10:1 ratio of matrix to sample, followed by heating the mixture to ca. 100 °C until a clear solution is formed. Upon cooling a small portion of this solid mixture is placed on a CaF₂ window. A second window is placed on top of he first and the sandwich is heated on a hotplate until the salt mixture melts. The plates are removed from the hotplate and gently compressed insuring a uniform sample upon cooling. Samples in bmim PF₆ are prepared as for Nujol and treated accordingly.

3. Results and discussion

3.1. Thiol bridged dimers

 $M_2(CO)_4(\mu$ -S-*t*-Bu)₂, where M = Rh or Ir, readily dissolve in Nujol to give deep red/brown solutions. IR spec-

Table 1 Photolysis of $M_2(CO)_4(\mu$ -S-t-Bu)₂ in Nujol at ca. 90 K

$Rh_2(CO)_4(\mu$ -S-t-Bu) ₂	2068 (a_1), 2048 (b_1), 1998 (b_2)
$Rh_2(CO)_3(\mu$ -S-t-Bu) ₂	2058, 1996, 1980
$Ir_2(CO)_4(\mu$ -S-t-Bu) ₂	2062 (a ₁), 2040 (b ₂), 1987 (b ₂)
$Ir_2(CO)_3(\mu$ -S-t-Bu) ₂	2056, 2001, 1993

Carbonyl stretching bands in cm⁻¹.

tra of these solutions at room temperature show carbonyl stretching bands at 2068, 2048, and 1998 cm^{-1} and 2062, 2040, and 1987 cm^{-1} for rhodium and iridium, respectively. Band positions and assignments are summarized in Table 1. Spectral assignments are based on those of Johnson, et al., for Rh₂(CO)₄(µ-SEt)₂ [3]. The band positions of the t-butyl thiol derivative agree to within experimental error with the positions of the ethyl thiol derivative. In contrast, the reported carbonyl stretching bands of $Rh_2(CO)_4(\mu$ -SPh)₂ are higher in energy than those of the alkylthiols reflective of a modest reduction of electron density on the sulfur atoms as a result of resonance interactions between sulfur and the phenyl rings [4]. Like $Rh_2(CO)_4(\mu$ -Cl)₂ these spectra are consistent with a molecule with C_{2v} symmetry, folded about the S-S axis. The molecular structures of $M_2(CO)_4(\mu$ -SPh), where M=Rh [5] and Ir, [6] have been reported to be isomorphous with two independent molecules. For the rhodium compound the bending angles of the molecules are $115.2(2)^{\circ}$ and $113.7(2)^{\circ}$, while for the iridium compound the angles are 115.2° and 114.7°. $Rh_2(CO)_4(\mu$ -SEt)₂ has a bending angle of 105.0(1)° [5a]. Folding about the bridging atoms is generally found for this class of compounds. For example, the closely related bimetallic species, $Rh_2(CO)_4(\mu$ -Cl)₂, $Rh_2(CO)_2(PMe_3)_2(\mu-SPh)_2$, and $Ir_2(CO)_2[P(OMe)_3]_2(\mu-$ S-t-Bu)₂ have angles of 124° [7], 113° [8], and 132° [9], respectively.

No photolysis of either $Ir_2(CO)_4(\mu$ -S-*t*-Bu)₂ or Rh₂(CO)₄(μ -S-*t*-Bu)₂ is observed upon irradiation in

Fig. 1. (a) Difference spectrum of 10 min photolysis (330 nm $< \lambda_{irr} < 400$ nm) of Ir₂(CO)₄(µ-S-*t*-Bu)₂ and initial spectrum. (b) Difference spectrum of 10 min photolysis (330 nm $< \lambda_{irr} < 400$ nm) of Rh₂(CO)₄(µ-S-*t*-Bu)₂ and initial spectrum. (c) Same as (b) with starting material cancelled.



the visible. In contrast, UV irradiation (330 nm < λ_{irr} < 400 nm) results in loss of the bands of starting material and appearance of new bands as shown in the difference spectra in Figs. 1(a) and (b), respectively. In both cases a band at 2132 cm⁻¹ assigned to free CO indicates loss of CO. Three carbonyl stretching bands may be observed for the photoproducts of the two compounds although the central band in the rhodium photoproduct overlaps with the b₁ band of the starting species. In Fig. 1(c) we have exactly cancelled out the starting bands to reveal the spectrum of the rhodium photoproduct. Back photolysis (λ_{irr} > 400 nm) of both the Rh and Ir samples cleanly reverses the observed photochemistry.

On the basis of the observed spectra it is not possible to discriminate between C_1 and C_s symmetries for the photoproduct since both point groups predict three IR active modes. Since it is generally believed that a weakly bound solvent molecule enters a site vacated by a carbonyl ligand, we propose that the photoproducts have C_1 symmetry retaining the square planar geometry about the metal atoms. This hypothesis is further supported by the observation of photoreversal in which the weakly bound alkane is photochemically displaced permitting re-complexation of CO.

These studies establish that both $Ir_2(CO)_4(\mu$ -S-*t*-Bu)_2 and Rh₂(CO)₄(μ -S-*t*-Bu)_2 undergo photolysis paralleling that of Rh₂(CO)₄(μ -Cl)_2. The carbonyl stretching frequencies of Rh₂(CO)₄(μ -S-*t*-Bu)_2 are about 45 cm⁻¹ lower than those of Rh₂(CO)₄(μ -Cl)₂ reflecting the somewhat better electron donating ability of the thiol ligands.

Both rhodium and iridium carbonyl thiol compounds undergo reaction with phosphines to form addition products that thermally undergo CO loss with retention of the bridge [10]. This contrasts with $Rh_2(CO)_4(\mu-Cl)_2$ for which bridge cleavage occurs even upon addition of amines. Further, the thiol derivatives are not observed to react with either amines or H_2 [11]. We are currently extending our photochemical studies to establish whether it is possible to photochemically prepare derivatives of the thiol bridged dimers with these and other ligands.

3.2. $[M(CO)_2Cl_2]^{l-}$ anions

Some years ago Geoffroy et al. [12] examined the UV/visible spectroscopy of $[Rh(CO)_2Cl_2]^{1-}$ and $[Ir(CO)_2Cl_2]^{1-}$ in the context of a broad investigation of the structure and bonding of square planar complexes. Utilizing electronic spectroscopy and circular dichroism, these authors assigned the lower energy absorption bands of the Rh and Ir anions to MLCT transitions arising from excitations from the metal $a_{1g}(z^2)$ and $b_{2g}(xy)$ orbitals to an a_{2u} orbital that is essentially CO π^* in character. Quite recently, Boyd and coworkers, have utilized dft calculations to explore the ground and excited

states of these anions and confirmed the earlier assignments with the further observation that the excited states are expected to have M–CO antibonding character. It is specifically noted that the B_1 state corresponding to the highest molar absorbtivity of the low energy transitions may lead to Rh–CO bond breaking.

To examine the photochemistry of these rhodium and iridium species we have utilized two ionic matrices, bmim PF₆ (bmim=1-butyl, 3-methylimidazolium) and NEt₃Oct PF₆. The former matrix has occasionally been found by us to undergo secondary reactions with photoproducts, while the latter matrix appears to be inert in all cases we have examined. In the current case the bmim cation does not appear to exhibit any unusual interaction with either Rh(CO)₂Cl₂^{1–} or its photoproduct.

IR spectra of [NBu₄][Rh(CO)₂Cl₂] and [NMe₄][Ir- $(CO)_2Cl_2$ in the ionic matrices are consistent with their cis geometries having two strong terminal carbonyl transitions. Spectral data is presented in Table 2. The obcarbonyl served stretching frequencies for $Rh(CO)_2Cl_2^{1-}$ are substantially lower than the values, $v_{sym} = 2135$ and $v_{asym} = 2058$ cm⁻¹, calculated by Boyd using CCSD(T)/6-331G(d) methods. Photolysis in the visible (λ_{irr} > 400 nm) resulted in no observed changes in the infrared spectra. Upon photolysis in the UV (330 nm < λ_{irr} < 400 nm) the bands of the anions were observed to decrease while two new bands grew in each sample as shown in Fig. 2. The high energy band at 2134 cm^{-1} is assigned to free CO in the NEt₃OctPF₆ matrix, thus, as predicted by theory, the primary photoprocess under these conditions is CO loss. The single, broad metal-carbonyl band requires that the photoproduct has one carbonyl. Back photolysis in the visible ($\lambda_{irr} > 400$ nm) results in clean reformation of the starting species. The photolysis of $[NBu_4][Rh(CO)_2Cl_2]$ in bmim PF₆ differs from that in NEt₃Oct PF₆ only in small shifts attributable to solvent effects.

Boyd and his coworkers propose on the basis of their dft calculations that the CO loss species, $Rh(CO)_2Cl_2^{1-}$, should have a T-type, C_{2v} , geometry. The calculated IR stretching frequency for this species using CCSD(T)/6-311G(d) methods is 1996 cm⁻¹, in remarkable agreement with the observed value. Our previous work with amine derivatives, $Rh(CO)_2(ammine)Cl$, in frozen Nujol reveals two carbonyl stretching bands in the photoproducts that we have assigned to CO-loss species in which the remaining

Table 2

Photolysis	of IR.	NIIM	$(CO)_{a}$	Cl _a l in	NEt _a Oct	PE _c at ca	90 K
FIIOLOIYSIS	$01 K_4$	11 N 1V1 (CO_{j_2}	C_{12} m	INEI3OCI	rr ₆ at ca.	90 K

$Rh(CO)_2Cl_2^{1-}$	2069, 1993
$Rh(CO)_2Cl_2^{-1-}$	1977
$Ir(CO)_2Cl_2^{1-}$	2051, 1970
$\operatorname{Ir}(\operatorname{CO})\operatorname{Cl}_2^{\overline{1}}$	1946

Carbonyl stretching bands in cm⁻¹.



Fig. 2. (a) Difference spectrum of 10 min photolysis (330 nm $< \lambda_{irr} < 400$ nm) of [NBu₄][Rh(CO)₂Cl₂] and starting material spectrum. (b) Difference spectrum of 10 min photolysis (330 nm $< \lambda_{irr} < 400$ nm) of [NBu₄][Ir(CO)₂Cl₂] and starting material spectrum.

CO is *trans* to either a chloride or ammine ligand. These observations require the CO-loss species to retain elements of its square planar geometry. In the current case, we suggest that the fourth coordination position is occupied by a weakly bound solvent molecule. This proposal is consistent with the observed back-photolysis which is believed to arise from the low energy displacement of a solvent molecule from the photointermediate permitting recombination with CO.

3.3. $Ir(CO)(PMe_3)_2Cl$

We note that for neither the rhodium nor iridium anions is there any suggestion of structural transformations corresponding to the tetragonal distortions we have observed for $Rh(CO)(PR_3)_2Cl$, where R = Me or Bu. In the case of the dicarbonyl anions, any species arising from tetragonal distortion would still have two carbonyl stretching bands and no such species is ob-



Fig. 3. (a) Spectrum of Ir(CO)(PMe₃)₂Cl in Nujol at ca. 90 K. (b) Difference of spectrum after 10 min photolysis ($\lambda_{irr} = 400 \pm 70$ nm and starting material spectrum.

the energy available upon visible irradiation (400

nm = 71 kcal/mol). In order to ascertain whether the tetragonal distortions observed for rhodium are also seen for iridium we have carried out the photolysis of Ir(CO)(PMe₃)₂Cl in Nujol and find that a new species does indeed appear, Fig. 3. The presence of small amounts of impurities believed to be either Ir(CO)₂(PMe₃)Cl or corresponding dimers, as seen by the small bands around 2024 cm⁻¹ complicate higher energy photolysis, but photolysis at $\lambda_{\rm irr} = 400 \pm 70$ nm clearly show loss of the band associated with Ir(CO)(PMe₃)₂Cl and growth of a new band at 1947 cm^{-1} . The absence of a band at 2132 cm^{-1} effectively rules out competition with CO-loss. The positions of the bands in Fig. 3 are reminiscent of, and indeed very close to, those observed for the rhodium compound. It appears that the very electron rich alkyl phosphine derivatives may be excited to a metastable state with tetragonal distortion, whereas the neutral ammine and anionic dichloride dicarbonyl derivatives, in which electron density is distributed between the two carbonyl ligands, have no comparable distortion. Finally, we note that a recent flash photolysis study of Ir(CO)(PPh₃)₂Cl has been interpreted in terms of a relatively long lived excited state species with a carbonyl stretching frequency close to that of the ground state [13]. It seems likely that the species observed in Nujol and that observed under flash conditions may well be related.

4. Conclusions

UV photolysis has been shown to initiate CO loss from thiol bridged rhodium and iridium bimetallic species as well as their closely related dicarbonyl dichloride anions. In the former case this appears to open new opportunities for ligand replacement chemistry involving amines and H_2 , whereas in the latter case the resulting monocarbonyl species may be capable of undergoing oxidative addition of H_2 and alkanes with potential application to photocatalysis.

In this context we note the highly relevant studies by Yates and coworkers of $Rh(CO)_2$ species on Al_2O_3 surfaces in which it has been found that photolysis generates what are believed to be Rh(CO) species and these species have been shown to undergo oxidative addition with H_2 [14], cyclohexane [15] and methane [16]. Photolysis of the $Rh(CO)_2$ species on alumina have been followed by IR and it has been shown that the initial carbonyl stretching bands at 2100 and 2030 cm⁻¹ are decreased while new bands appear at about 2060 and 1975 cm⁻¹. The terminal carbonyl stretching bands of the *gem*-dicarbonyl species are somewhat high reflecting the likelihood that the Rh is bound to an oxo ligand. The 2060 cm⁻¹ band is attributed to an Rh₂(CO)₂ species, while the 1975 cm⁻¹ band is assigned to a Rh(CO) species [17]. The assignment of this latter band is quite consistent with the observations made in the current work. Our own studies of the photolysis of Rh(CO)₂(L)CL species, where L is a propyl amine bound to the surface of MCM-41 mesoporous silica, in which monocarbonyl species are formed will be reported in due course [18].

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