

Luminescent Alkyl Complexes of Iridium

Prudence Bradley, Curtis E. Johnson, and Richard Eisenberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627, U.S.A.

A series of luminescent alkyl complexes of formula $\text{IrR}(\text{CO})\text{L}_2(\text{mnt})$, where mnt = maleonitriledithiolate, $\text{R} = \text{Me, Et, Pr, and CH}_2\text{CN}$, and L is a triarylphosphine, have been characterized; photolysis of $\text{IrMe}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$ shows that Ir-Me bond homolysis is favoured strongly over CO photo-dissociation.

In this report we describe the characterization and photochemistry of a series of iridium alkyl carbonyl complexes which are among the first transition metal alkyl complexes found to luminesce in fluid solution.¹ Our study reveals that Ir-C bond homolysis is favoured photochemically over CO dissociation in these systems, thereby contrasting with recent results reported for the benzyl carbonyl complex $(\text{cp})\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}_6\text{H}_5)$ ($\text{cp} = \eta^5\text{-cyclopentadienyl}$).²

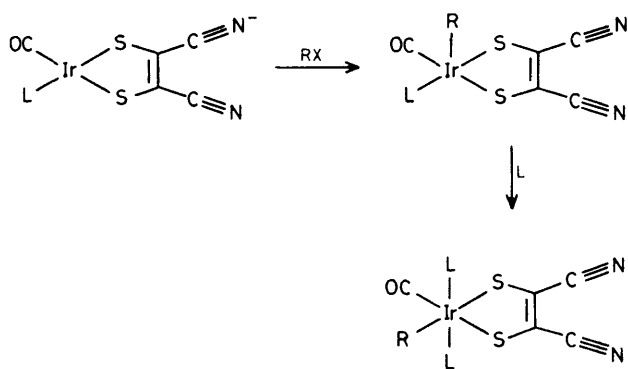
The complexes $\text{IrR}(\text{CO})\text{L}_2(\text{mnt})$ (**1**)–(**4**) (mnt = maleonitriledithiolate), were prepared by the oxidative addition of RX to the corresponding iridium(I) complex, $\text{Ir}(\text{CO})\text{L}(\text{mnt})^-$, followed by the addition of L as shown in Scheme 1. Yields were typically >85%. For (**1d**)–(**f**), the starting Ir^{I} complex was generated *in situ* from $\text{Ir}(\text{CO})_2(\text{mnt})^-$ and 1 equivalent of L . The complexes were characterised by ^1H n.m.r., i.r., and electronic spectroscopy,[†] and elemental analyses, and the

structural assignment of (**1a**) was confirmed by a single crystal X-ray structure determination.[‡]

As shown in Figure 1, $\text{IrMe}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$ (**1a**) possesses an octahedral co-ordination geometry with *trans* PPh_3 ligands, and the methyl and CO groups *trans* to the sulphur atoms of the bidentate mnt ligand. The triplet splitting exhibited by the methyl resonance of (**1a**) is also observed in the spectra of the other alkyl phosphine complexes with J_{PH} of ca. 3.6 Hz, indicating a similar octahedral geometry with equivalent phosphine donors. Complex (**1f**), however, exhibits two singlets for the CNBu^t ligands and a chemical shift for the Me resonance suggestive of a different ligand arrangement for the octahedral co-ordination geometry. All of the complexes (**1**)–(**4**) show similar electronic spectra with two bands in the ranges 415–420 and 380–385 nm with ϵ values of 10^3 – 10^4 .

[†] ^1H n.m.r. in CDCl_3 of (**1a**)–(**4a**) show a characteristic multiplet pattern for the phenyl protons in the δ 7.0–7.8 range, for alkyl ligand: (**1a**), 0.39 t (J_{PH} 3.7 Hz); (**2a**), 2.69 m, 0.68 t (J_{HH} 7.3 Hz); (**3a**), 1.29 m, 0.92 m, 0.05 t (J_{HH} 6.8 Hz); (**4a**), 1.58 t (J_{HH} 4.5 Hz). Chemical shifts for the other methyl compounds are: (**1b**), 0.35 t; (**1c**), 0.34 t; (**1d**), 0.36 t; (**1e**), 0.39 t; all J_{PH} are 3.6 Hz. ^1H n.m.r. for (**1f**); Bu^tNC 1.58 s, 1.50 s, Me, 0.64 s. I.r. in KBr exhibit ν_{CN} at ca. 2200 cm^{-1} for all compounds. Electronic spectra in MeCN [λ/nm ($\epsilon/\text{l mol}^{-1}\text{ cm}^{-1}$)]: (**1a**), 421 (4100); (**2a**), 383 (3500), 434sh (1700); (**3a**), 391 (2800), 421sh (2400); (**4a**), 384 (2900), 417 (2600); (**1b**), 419 (3900), 442sh (3100); (**1c**), 386 (3700), 420 (3800); (**1d**), 417 (3400); (**1e**), 412 (4300), 426 (4000); (**1f**), 380 (3400), 406 (3700).

[‡] Crystal data for (**1a**): triclinic space group $P\bar{1}$, $a = 13.178(4)$, $b = 13.670(4)$, $c = 12.592(2)$ Å, $\alpha = 105.03(2)$, $\beta = 115.42(2)$, $\gamma = 95.72(2)^\circ$, $U = 1919.9$ Å³; $Z = 2$, $D_c = 1.557$ g cm^{-3} . Data were collected on an Enraf-Nonius CAD4 diffractometer, $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å); 6298 unique reflections ($h, \pm k, \pm l$, $4^\circ < 2\theta < 45^\circ$). The SDP+ computer programs were used for data reduction, structure solution and least-squares refinement with convergence at $R_1 = 0.020$, $R_2 = 0.028$ and G.O.F. = 1.09 [451 variables, 5632 reflections with $I > 3\sigma(I)$, all non-hydrogen atoms anisotropic, phenyl hydrogens calculated and fixed]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



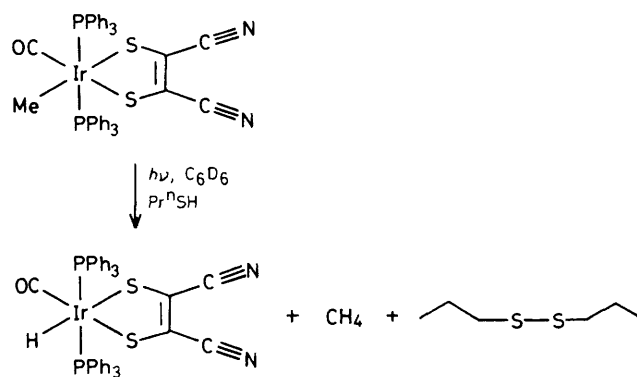
Scheme 1.	R	L	$\nu(\text{CO})/\text{cm}^{-1}$
(1a)	Me	PPh_3	2017
(1b)	Me	$\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$	2011
(1c)	Me	$\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3$	2027
(1d)	Me	$\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$	2020
(1e)	Me	$\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$	2016
(1f)	Me	Bu^tNC	2061
(2a)	Et	PPh_3	2015
(3a)	Pr^n	PPh_3	2015
(4a)	CH_2CN	PPh_3	2045

Complexes (1)–(4) luminesce in solution at room temperature. § The emission spectra for these complexes show vibrational structure which sharpens at lower temperatures in rigid media as shown in Figure 2 for $\text{IrMe}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$ (1a). The structuring corresponds to a vibrational progression of *ca.* 1100 cm^{-1} , and is reminiscent of that reported previously for the four-co-ordinate d^8 complexes $\text{MLL}'(\text{mnt})^n$ ($M = \text{Ir}, \text{Rh}, n = 1$; $M = \text{Pt}, n = 0$).³ The emission maxima for the Me compounds vary with the electron donating ability of the phosphine ligands, ranging from 695 nm for (1d) to 713 nm for (1e). Based on the emission structure and the red-shifting of the emission maxima with increasing ligand donor ability, we assign the emitting state as a $(d-\pi^*_{\text{mnt}})$ metal-to-ligand charge transfer.

When a benzene solution of (1a) is photolysed using a medium pressure Hg arc lamp and a 350–500 nm bandpass filter, starting material (90%) is recovered after 24 h along with small amounts of toluene and $\text{IrH}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$ (5). ¶ However, photolysis of (1a) in the presence of Pr^nSH (5–10 equiv.), a radical trap which does not quench the luminescence, yields stoichiometric formation of CH_4 , di-n-propyl disulphide, and the hydride complex (5) within 3 h (Scheme 2). Control samples of (1a) and Pr^nSH in benzene in the dark produced no reaction chemistry at ambient temperatures and less than 5% conversion to CH_4 after 48 h of heating at 75°C. In benzene with CDBr_3 (*ca.* 50 equiv.) added, photolysis of (1a) leads to its disappearance within 55 min and formation of MeBr and $\text{IrBr}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$, while photolysis with 3 equivalents of 4-hydroxy-Tempo (4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy) free radical yields complete conversion into the 4-hydroxy-Tempo methyl ether. The quantum yield for Ir–Me cleavage using Pr^nSH (400 equiv.)

§ Luminescence data in CHCl_3 at 25°C in cm^{-1} (vibrational spacing): (1a), 14030, 12990 (1040); (1b), 14050, 13020 (1030); (1c), 14350, 13070 (1280); (1d), 14390, 13070 (1320); (1e), 14030, 13070, (960); (1f), 14050, 13060, (990); (2a), 14180, 13020 (1160); (3a), 14090, 13060 (1030); (4a), 14490, 13110 (1380).

¶ Compound (5): δ (J_{PIH} , Hz) of hydride resonance (400 MHz, CDCl_3), -10.24 t (10.6); i.r. in KBr ($\nu_{\text{CO}}, \nu_{\text{IH}}, \nu_{\text{CN}}, \text{cm}^{-1}$), 2039, 2140, *ca.* 2200.



Scheme 2

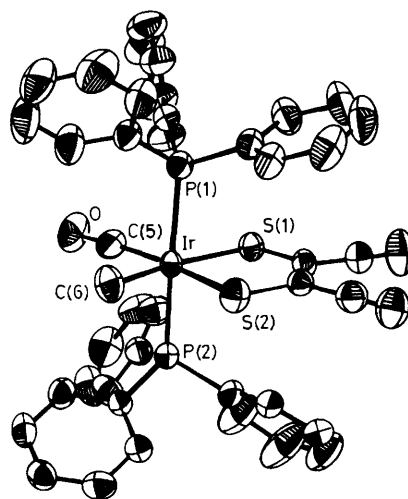


Figure 1. ORTEP diagram of $\text{IrMe}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$. Some selected bond distances (Å) and angles ($^\circ$). Ir–C(6), 2.165; Ir–S(1), 2.442; Ir–S(2), 2.373; Ir–P(1), 2.392; Ir–P(2), 2.394; Ir–C(5), 1.86; C(5)–O, 1.131. C(5)–Ir–C(6), 86.3; S(1)–Ir–S(2), 87.7; S(1)–Ir–C(5), 105.9; O–C(5)–Ir, 174.1; P(1)–Ir–P(2), 172.6.

was determined to be 4.5×10^{-3} . These results suggest photochemical homolysis of the Ir–Me bond which reforms readily in the absence of a radical trap.

In order to establish whether CO dissociation was competing photochemically with Ir–Me homolysis, the photolysis of (1a) was performed in the presence of ^{13}CO (200 torr) and Pr^nSH (6 equiv.).** After 5 min of photolysis, CH_4 was observed with no evidence of photochemically promoted ^{13}CO incorporation into (1a), and after 25 min no starting material remained and no ^{13}CO was incorporated into the product (5) as is apparent from ^{13}C n.m.r. spectroscopy. This result contrasts with that reported for the system $(\text{cp})\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}_6\text{H}_5)$ in which CO loss is the principal photochemical process.² Thermal reaction with CO does occur with (1a) more slowly and at higher CO pressures to form $\text{Ir}(\text{COMe})(\text{CO})(\text{PPh}_3)(\text{mnt})$ analogous to rhodium acyl complexes reported previously.⁴ This reaction is concurrent with slow thermal CO exchange but neither process is promoted by light. The slowness of ^{13}CO incorporation into (1a) and the

** Photolyses were followed by ^{13}C n.m.r. spectroscopy at 75 MHz; spectra were undecoupled to minimize acyl formation by sample heating.

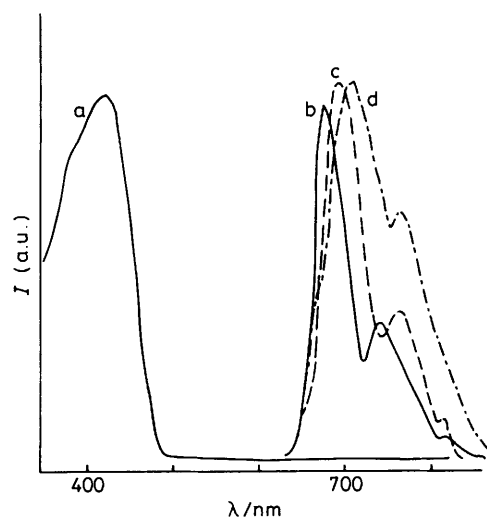


Figure 2. Emission and absorption spectra of $\text{IrMe}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$; intensity expressed in arbitrary units. A is the electronic absorption in acetonitrile at ambient temperature; B, C, and D are emission spectra with λ_{ex} at 440 nm; B, ether-pentane-alcohol glass at 77 K; C, solid at 77 K; D, CHCl_3 solution at ambient temperature.

lack of photochemical exchange are remarkable in view of the fact that tertiary phosphine exchange into (1a) occurs readily at room temperature *in the dark*. This exchange is too rapid to measure by conventional kinetics techniques.

The photochemistry of the Ir-Et complex (2a) was also studied under analogous conditions. Photolysis of (2a) in benzene quantitatively produces ethylene and (5) in 5 min. This example of β -elimination, which is also seen with the propyl complex (3a), only occurs upon photolysis despite facile tertiary phosphine exchange in the dark at 25°C. Photolysis of (2a) in the presence of ^{13}C O (200 torr) shows no label incorporation into either starting material or the product hydride (5), indicating that dissociation of CO is not the primary photochemical process. However, attempts to trap Et^\cdot using either Bu^\cdotSH or CDBr_3 have not been successful,

and photolysis of (2a) in the presence of ^{13}C O (230 torr) and Bu^\cdotSH (60 equiv.) has yielded only ethylene and (5), again without label incorporation. The reaction chemistry of (2a) is further complicated by slower thermal chemistry leading to acyl formation. For example, (2a) alone or in the presence of Bu^\cdotSH is converted into $\text{Ir}(\text{COEt})(\text{PPh}_3)_2(\text{mnt})$ completely within 24 h at 25°C, while at 80°C conversion is complete within 15 min. What seems clear, however, is that the β -elimination observed for (2a) and (3a) is photochemically promoted, and involves radical formation by Ir-R bond cleavage.

Complexes (1)–(4) are thus among the first luminescent alkyl complexes, and as shown definitively for (1a), their principal mode of photochemical reactivity is M-C bond homolysis and not CO dissociation.

We thank the National Science Foundation (CHE 86-03055) and the Office of Naval Research for support of this work, and Johnson Matthey Co., Inc. for a generous loan of iridium salts.

Received, 22nd September 1987; Com. 1381

References

- Recent reviews on alkyl complex photochemistry include: D. B. Pourceau and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1985, **24**, 249; H. G. Alt, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 766. A luminescent Pt alkyl complex has been reported: L. Chassot, A. von Zelewsky, D. Sandrini, M. Maestri, and V. Balzani, *J. Am. Chem. Soc.*, 1986, **108**, 6084. Luminescent aryl complexes in which the aryl group is part of a chelate ring have been reported: K. A. King and R. J. Watts, *J. Am. Chem. Soc.*, 1987, **109**, 1589.
- J. P. Blaha and M. S. Wrighton, *J. Am. Chem. Soc.*, 1985, **107**, 6531; A. F. Hepp, J. P. Blaha, C. Lewis, and M. S. Wrighton, *Organometallics*, 1984, **4**, 174.
- C. E. Johnson, R. Eisenberg, T. R. Evans, and M. Burberry, *J. Am. Chem. Soc.*, 1983, **105**, 1795.
- C.-H. Cheng, B. D. Spivack, and R. Eisenberg, *J. Am. Chem. Soc.*, 1977, **99**, 3003; C.-H. Cheng and R. Eisenberg, *Inorg. Chem.*, 1979, **18**, 1418.

|| (1a) and (4a) do not form acyls even if heated for extended periods.