

## Rhenium(VI) Benzyldiyne Complexes, $\text{Re}(\equiv\text{C}-2,4,6\text{-C}_6\text{H}_2\text{Me}_3)(\text{PPh}_3)(\text{H}_2\text{O})\text{X}_3$ ( $\text{X} = \text{Cl}$ and $\text{Br}$ ): Crystal Structure and Spectroscopic Properties

Wen-Mei Xue,<sup>†</sup> Michael C. W. Chan,<sup>†</sup>  
Thomas C. W. Mak,<sup>‡</sup> and Chi-Ming Che<sup>\*,†</sup>

Departments of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, and The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Received March 21, 1997

### Introduction

While the photochemistry of  $d^2$  metal complexes containing metal–ligand multiple bonds has been documented,<sup>1–4</sup> studies on corresponding  $d^1$  complexes are rare. The possibility of producing long-lived excited states from such species was suggested by Winkler and Gray in detailed spectroscopic work on the molybdenyl(V) ion,<sup>5</sup> and fluorescence from an oxomolybdenum(V) moiety has been investigated by Mohammed and Maverick.<sup>6</sup> However, reports on emissive rhenium(VI) complexes are scarce,<sup>7</sup> although the electronic structure of the first  $d^1$  *trans*-dioxo complex, *trans*- $[\text{ReO}_2(\text{dmap})_4][\text{PF}_6]_2$  (*dmap* = 4-(dimethylamino)pyridine), was presented by Gray et al.<sup>8</sup>

The rhenium(V) benzyldiyne complexes  $\text{Re}^{\text{V}}(\equiv\text{CAr})(\text{CO})_2\text{X}_2(\text{py})$  ( $\text{Ar}' = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$ ;  $\text{X} = \text{Cl}$ ,  $\text{O}-2,6\text{-C}_6\text{H}_3\text{Pr}_2$ ) have been prepared by Williams and Schrock,<sup>9</sup> while we recently described the photoluminescence and photoredox properties of related derivatives, including  $[\text{Re}^{\text{V}}(\equiv\text{CAr})(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})\text{Cl}]\text{ClO}_4$ .<sup>10</sup> Using the latter as precursor, we now report the synthesis of  $\text{Re}^{\text{VI}}(\equiv\text{CAr})(\text{PPh}_3)(\text{H}_2\text{O})\text{Cl}_3$  and  $\text{Re}^{\text{VI}}(\equiv\text{CAr})(\text{PPh}_3)(\text{H}_2\text{O})\text{Br}_3$ , which are the first examples of emissive  $d^1$  complexes containing a metal–carbon multiple bond.

### Experimental Section

**Physical Measurements.** Infrared spectra were recorded with KBr disks on a Nicolet 20FXC FT-IR spectrophotometer. UV–visible absorption spectra were obtained on a Milton Roy Spectronic 3000 diode array spectrophotometer. Elemental analyses were performed by Butterworth Laboratories (UK). Mass spectra were obtained on a Finnigan Mat 95 fast atom bombardment mass spectrometer. Magnetic moment measurements were performed with solid crystalline samples using a CAHN 2000 magnetobalance in the temperature range 75–

300 K. Data were corrected for diamagnetism using Pascal's constants ( $-3.50 \times 10^{-4}$  and  $3.93 \times 10^{-4}$  emu mol<sup>-1</sup> for **2** and **3**, respectively). Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 175 universal programmer and a Model 273 potentiostat coupled to a Kipp & Zoner X–Y recorder. A conventional two-compartment cell was used with  $\text{Ag}/\text{AgNO}_3$  (0.1 mol dm<sup>-3</sup> in acetonitrile) as the reference electrode. The supporting electrolyte was  $[\text{Bu}_4\text{N}][\text{PF}_6]$  (0.1 mol dm<sup>-3</sup>). Glassy carbon was used as the working electrode.

Steady state emission spectra were recorded on a SPEX 1681 Fluorolog-2 series F111AI spectrometer. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability. Emission quantum yields were measured in deoxygenated solution using the method of Denas and Crosby with aqueous quinine sulfate as reference.<sup>11</sup> Emission lifetimes were determined with a Quanta Ray DCR-3 Nd–YAG laser (pulse output 355 nm, 8 ns) in deoxygenated solutions. The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix Model 2430 digital oscilloscope.

Stern–Volmer quenching experiments were carried out in deoxygenated *N,N*-dimethylformamide solutions of the metal complex in the presence of the quenchers [Q]. In each case, a linear plot of  $\tau_0/\tau$  versus [Q] was obtained, from which second-order quenching rate constants,  $k_q$ , were deduced according to the equation  $\tau_0/\tau = 1 + k_q\tau_0[\text{Q}]$ , where  $\tau_0$  and  $\tau$  refer to the emission lifetimes in the absence and presence of [Q].

**Synthesis.  $\text{Re}^{\text{VI}}(\equiv\text{CAr})(\text{PPh}_3)(\text{H}_2\text{O})\text{Cl}_3$  (**2**).**  $[\text{Re}^{\text{V}}(\equiv\text{CAr})(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})\text{Cl}]\text{ClO}_4$  (**1**)<sup>10</sup> (100 mg, 0.1 mmol) was dissolved in chloroform (20 cm<sup>3</sup>), and excess aqueous concentrated HCl (2 cm<sup>3</sup>, 12 mol dm<sup>-3</sup>) was added. The yellow solution was refluxed for 5 days to give a green solution. The organic layer was separated and dried with  $\text{MgSO}_4$  and then evaporated to dryness *in vacuo*. The crude product was recrystallized from dichloromethane/petroleum ether (40–60 °C) to give yellow-green crystals (yield 60 mg, 85%). Anal. Calcd for  $\text{C}_{28}\text{H}_{28}\text{OCl}_3\text{PRe}$ : C, 47.78; H, 3.98. Found: C, 48.15; H, 3.87. FAB MS ( $m/z$ ): 703 ( $\text{M}^+$ ), 685 ( $\text{M}^+ - \text{H}_2\text{O}$ ), 650 ( $\text{M}^+ - \text{H}_2\text{O} - \text{Cl}$ ). IR ( $\text{cm}^{-1}$ ):  $\nu$  1436 ( $\text{Re}=\text{C}$ ).

**$\text{Re}^{\text{VI}}(\equiv\text{CAr})(\text{PPh}_3)(\text{H}_2\text{O})\text{Br}_3$  (**3**).** A solution of **1** (100 mg, 0.1 mmol) in dried and deoxygenated dibromomethane (50 cm<sup>3</sup>) was irradiated with UV–visible light (Model RPR-100 Rayonet photochemical chamber reactor equipped with 16 8-W RPR 3500-Å Hg lamps) for 30 h at room temperature. The green solution was evaporated to dryness *in vacuo*. The crude product was recrystallized from dichloromethane/petroleum ether (40–60 °C) to give a pale green crystalline solid (yield 65 mg, 78%). Anal. Calcd for  $\text{C}_{28}\text{H}_{28}\text{OBr}_3\text{PRe}$ : C, 40.13; H, 3.34. Found: C, 40.35; H, 3.35. FAB MS ( $m/z$ ): 837 ( $\text{M}^+$ ). IR ( $\text{cm}^{-1}$ ):  $\nu$  1437 ( $\text{Re}=\text{C}$ ).

**X-ray Crystallography.** A yellow-green prism crystal of **2** with dimensions 0.10 × 0.20 × 0.30 mm was used for X-ray analysis. Intensity data were collected using graphite crystal monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Rigaku AFC7R diffractometer, using variable rate  $\omega$  scan at 294 K. Of the 4883 unique reflections measured ( $4^\circ \leq 2\theta \leq 50^\circ$ ,  $+h, +k, \pm l$ ), 3733 were considered observed ( $F > 4\sigma(F)$ ). The structure was solved by direct methods and subsequently refined by full-matrix least-squares using the Siemens SHELXTL PLUS (PC Version).<sup>12</sup> Final cycle of blocked-cascade least-squares refinement: maximum and minimum peaks in difference Fourier map = +0.88 and -0.95 e Å<sup>-3</sup>. Crystallographic data:  $\text{C}_{28}\text{H}_{28}\text{OCl}_3\text{PRe}$ , fw = 703.8, monoclinic,  $P2_1/n$ ,  $a = 11.907(2)$  Å,  $b = 15.750(3)$  Å,  $c = 14.763(3)$  Å,  $\beta = 90.53(3)^\circ$ ,  $V = 2768.5(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.689$  g cm<sup>-3</sup>,  $\mu$  (Mo K $\alpha$ ) = 4.76 mm<sup>-1</sup>,  $R = 0.033$ ,  $R_w = 0.039$ , GOF = 1.28.

### Results and Discussion

The air-stable rhenium(VI) benzyldiyne derivatives  $\text{Re}^{\text{VI}}(\equiv\text{CAr})(\text{PPh}_3)(\text{H}_2\text{O})\text{X}_3$  ( $\text{X} = \text{Cl}$  (**2**) and  $\text{Br}$  (**3**)) are prepared from  $\text{Re}^{\text{V}}(\equiv\text{CAr})(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})\text{Cl}]\text{ClO}_4$  (**1**) by thermal

<sup>†</sup> The University of Hong Kong.

<sup>‡</sup> The Chinese University of Hong Kong.

- (1) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346. (b) Thorp, H. H.; Houten, J. V.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889.
- (2) Neyhart, G. A.; Bakir, M.; Boaz, J.; Vining, W. J.; Sullivan, B. P. *Coord. Chem. Rev.* **1991**, *111*, 27.
- (3) (a) Che, C. M.; Lau, T. C.; Lam, H. W.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1989**, 114. (b) Che, C. M.; Lam, H. W.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1529. (c) Che, C. M.; Lam, H. W.; Tong, W. F.; Lai, T. F.; Lau, T. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1883. (d) Yam, V. W. W.; Che, C. M. *Coord. Chem. Rev.* **1990**, *97*, 93.
- (4) Goll, J. G.; Liu, W.; Thorp, H. H. *J. Am. Chem. Soc.* **1993**, *115*, 11048.
- (5) Winkler, J. R.; Gray, H. B. *Comments Inorg. Chem.* **1981**, *1*, 257.
- (6) Mohammed, A. K.; Maverick, A. W. *Inorg. Chem.* **1992**, *31*, 4441.
- (7) Maverick, A. W.; Yao, Q.; Mohammed, A. K.; Henderson, L. J., Jr. *Photosensitive Metal-Organic Systems*; ACS Advances in Chemistry Series 238; American Chemical Society: Washington, DC, 1993; Chapter 7, p 131.
- (8) Brewer, J. C.; Thorp, H. H.; Slagle, K. M.; Brudvig, G. W.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 3171.
- (9) Williams, D. S.; Schrock, R. R. *Organometallics* **1994**, *13*, 2101.
- (10) Xue, W. M.; Wang, Y.; Mak, T. C. W.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 2827.

(11) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(12) *SHELXTL-PC User manual*; Siemens Analytical Instruments: Madison, WI, 1990.

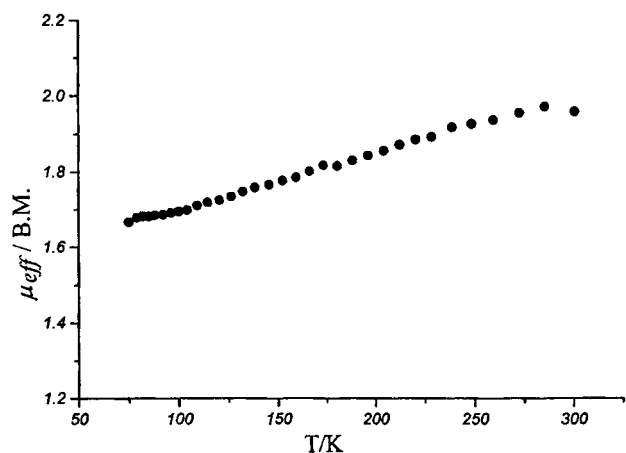


Figure 1. Effective magnetic moment ( $\mu_{\text{eff}}$ ) versus temperature for **2**.

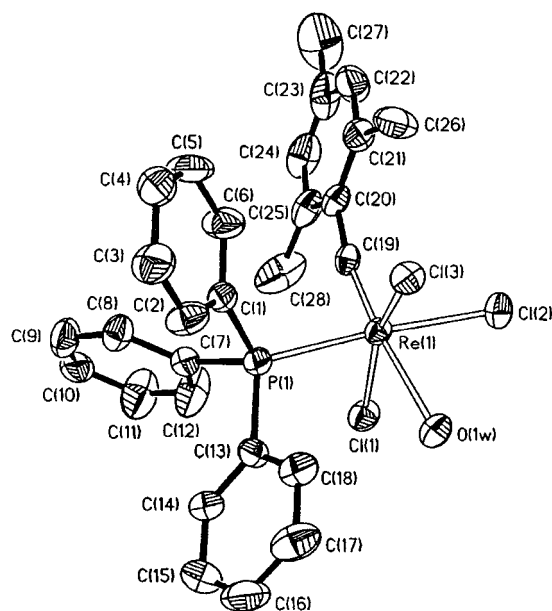


Figure 2. Perspective view of  $\text{Re}(\equiv\text{CAR}')(\text{PPh}_3)(\text{H}_2\text{O})\text{Cl}_3$  (**2**).

reaction with HCl in  $\text{CHCl}_3$  and by photooxidation in  $\text{CH}_2\text{Br}_2$ , respectively. The only reported examples of rhenium(VI) alkyldiene complexes are  $\text{Re}^{\text{VI}}(\equiv\text{CMe}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{X}_2$  ( $\text{X} = \text{Cl}$ , Br, and I).<sup>13</sup> Complex **2** is also formed by photolysis of **1** in deoxygenated dichloromethane or chloroform with UV-visible light ( $\lambda > 300$  nm), but the reaction time is increased ( $>5$  days). This is in accordance with the greater tendency for  $\text{CH}_2\text{Br}_2$  to be reduced compared to  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ .<sup>14a</sup>

Photooxidation of metal complexes in halogenated solvents is well established.<sup>14</sup> However, the treatment of **1** with HCl in chloroform to yield the benzylidene species **2** is unusual. We have found that the reaction can be performed under aerobic conditions, so the oxidant is likely to be molecular oxygen and/or the acid. No reaction is observed after refluxing **1** in

Table 1. Selected Bond Distances (Å) and Angles (deg) for **2**

Re—Cl(1)	2.348(2)	Re—P(1)	2.476(2)
Re—Cl(2)	2.436(2)	Re—C(19)	1.738(6)
Re—Cl(3)	2.351(2)	C(19)—C(20)	1.442(9)
Re—O(1w)	2.320(4)		
Cl(1)—Re—Cl(2)	90.5(1)	Cl(3)—Re—P(1)	88.0(1)
Cl(1)—Re—Cl(3)	158.8(1)	O(1w)—Re—P(1)	93.6(1)
Cl(2)—Re—Cl(3)	90.5(1)	Cl(1)—Re—C(19)	100.2(2)
Cl(1)—Re—O(1w)	78.5(1)	Cl(2)—Re—C(19)	91.8(2)
Cl(2)—Re—O(1w)	81.3(1)	Cl(3)—Re—C(19)	100.9(2)
Cl(3)—Re—O(1w)	80.8(1)	O(1w)—Re—C(19)	172.9(2)
Cl(1)—Re—P(1)	89.1(1)	P(1)—Re—C(19)	93.3(2)
Cl(2)—Re—P(1)	174.9(1)	Re—C(19)—C(20)	169.7(5)

Table 2. Photophysical Data for **2** and **3** in Dichloromethane at Room Temperature<sup>a</sup>

complex	UV-vis		emission		
	$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )	$E_{\text{em}}$ (nm)	$\phi_{\text{em}}^b$	$\tau^c$ ( $\mu\text{s}$ )
$\text{Re}^{\text{VI}}(\equiv\text{CAR}')(\text{PPh}_3)(\text{H}_2\text{O})\text{Cl}_3$ ( <b>2</b> )	315	9650	696	$7 \times 10^{-4}$	0.49
	410	1260			
	550	80			
	658	60			
$\text{Re}^{\text{VI}}(\equiv\text{CAR}')(\text{PPh}_3)(\text{H}_2\text{O})\text{Br}_3$ ( <b>3</b> )	330	6080	728	$6 \times 10^{-3}$	0.41
	386	3530			
	435	770			
	558	180			
	696	90			

<sup>a</sup> Concentration of complexes is in the range  $10^{-4}$ – $10^{-5}$  mol  $\text{dm}^{-3}$ .

<sup>b</sup> Quantum yields  $\pm 20\%$ . <sup>c</sup> Lifetimes  $\pm 10\%$ .

chloroform only for 5 days; thus, HCl is evidently needed. This transformation sharply contrasts with the reaction of tungsten and osmium alkyldiene complexes with HCl to yield the corresponding alkyldiene derivatives.<sup>15</sup>

The paramagnetic nature of **2** and **3** was confirmed by magnetic measurements. Figure 1 shows the effective magnetic moment ( $\mu_{\text{eff}}$ ) of **2** in the temperature range 75–300 K. The  $\mu_{\text{eff}}$  values of **2** and **3** at 300 K are 1.96 and 1.90  $\mu_{\text{B}}$ , respectively, which approaches the theoretical value of 1.73  $\mu_{\text{B}}$  for a  $d^1$  system. By comparison,  $\mu_{\text{eff}}$  for  $\text{Re}^{\text{VI}}(\equiv\text{CMe}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2$  increases from 1.55 to 1.65  $\mu_{\text{B}}$  as the temperature is lowered from 300 to 10 K.<sup>13</sup>

The molecular structure of **2** is shown in Figure 2, and selected bond distances and angles are presented in Table 1. The Re—C(19) distance of 1.738(6) Å is typical for a rhenium-carbon triple bond,<sup>16</sup> and the Re—C(19)—C(20) angle ( $169.7(5)^\circ$ ) is almost linear. Besides the rhenium examples already mentioned,<sup>13</sup> there are few reports concerning  $d^1$  alkyldiene complexes. The X-ray structure of *trans*-[MoF(≡CCH<sub>2</sub>Bu)(dppe)<sub>2</sub>][BF<sub>4</sub>] (dppe = 1,2-bis(diphenylphosphino)ethane) was described by Pombeiro and co-workers,<sup>17</sup> while Hopkins and co-workers synthesized [W(≡CPh)(dmpe)<sub>2</sub>Br][PF<sub>6</sub>] (dmpe = 1,2-bis(dimethylphosphino)ethane) by oxidation of W(≡CPh)(dmpe)<sub>2</sub>Br with [C<sub>7</sub>H<sub>7</sub>][PF<sub>6</sub>].<sup>18</sup> In contrast, the dimeric diamagnetic complex [W<sub>2</sub>(≡CPMe<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>Cl<sub>4</sub>][AlCl<sub>4</sub>]<sub>2</sub> was prepared by Schrock and co-workers through oxidation of W(≡CH)Cl(PMe<sub>3</sub>)<sub>4</sub> with C<sub>2</sub>Cl<sub>6</sub> and AlCl<sub>3</sub>.<sup>19</sup> The reactive 17-electron benzylidene intermediate [Mo(≡CPh)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>]-Cl was proposed in the photooxidation of Mo(≡CPh)(η<sup>5</sup>-

(13) Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jakobi, R.; Gütllich, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 334.

(14) (a) Bock, C. R.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 1309. (b) Miessler, G. L.; Zoebisch, E.; Pignolet, L. H. *Inorg. Chem.* **1978**, *17*, 3636. (c) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1981**, *103*, 1559. (d) Carter, J. D.; Kingsbury, K. B.; Wilde, A.; Schoch, T. K.; Leep, C. J.; Pham, E. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 2947. (e) Lindsay, E.; Malkhasian, A. Y. S.; Langford, C. H. *Inorg. Chem.* **1994**, *33*, 944.

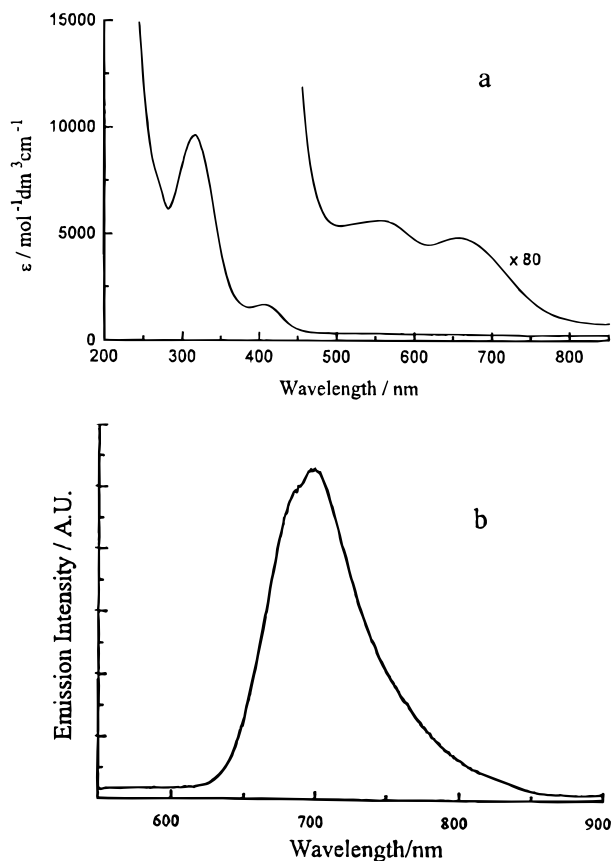
(15) For W: Mayr, A.; Asaro, M. F.; Kjelsberg, M. A.; Lee, K. S.; Van Engen, D. *Organometallics* **1987**, *6*, 432. For Os: Clark, G. R.; Cochrane, C. M.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1986**, *315*, 211.

(16) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; Fischer, H., Hoffman, P., Freissl, F. R., Schrock, R. R., Schubert, U., Weiss, K., Eds.; VCH Verlagsgesellschaft: Weinheim, 1988; p 147ff.

(17) Lemos, M. A. N. D. A.; Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1992**, *434*, C6.

(18) Manna, J.; Gilbert, T. M.; Dallinger, R. F.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5870.

(19) Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476.



**Figure 3.** UV-visible absorption (a) and emission (b,  $\lambda_{\text{ex}} = 658 \text{ nm}$ ) spectra of **2** ( $5.6 \times 10^{-5} \text{ mol dm}^{-3}$ ) in  $\text{CH}_2\text{Cl}_2$  at room temperature.

$\text{C}_5\text{H}_5(\text{P}(\text{OMe})_3)_2$  in chloroform or dichloromethane in the presence of  $\text{PMe}_3$ .<sup>14d</sup>

The photophysical data for **2** and **3** are summarized in Table 2. The UV-visible absorption spectrum of **2** (Figure 3a) exhibits a high-energy peak at 315 nm, a low-energy shoulder in the 410–450-nm region, and two weak bands at 550 and 658 nm, with molar absorptivities less than  $100 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ . Complex **3** displays similar absorptions in the 400–750-nm range, but there are more signals at 300–400 nm. Indeed, the lowest energy bands for **2** and **3** (at 658 and 696 nm, respectively) have absorptivities comparable to that for the spin-allowed  ${}^2\text{B}_2[(d_{xy})^1] \rightarrow {}^2\text{E}[(d_{xz}, d_{yz})^1]$  transitions of the  $d^1$   $[\text{MoOX}_4(\text{CH}_3\text{CN})]^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes, which are thought to be localized on the  $\text{MoO}^{3+}$  unit.<sup>6</sup> The electronic structures of the  $d^1$  complexes  $\text{trans}[\text{ReO}_2(\text{dmap})_4]^{2+}$ <sup>8</sup> and  $[\text{W}(\equiv\text{CPh})(\text{dmpe})_2\text{Br}]^+$ <sup>18</sup> have been discussed, and in both cases the HOMO was proposed to be the metal  $d_{xy}$  orbital (metal–ligand multiple bond taken as  $z$  axis), which is nonbonding with respect to the oxo and benzyldiyne ligands. Extensive spectroscopic studies<sup>1a</sup> have revealed that, in the  $d^1$  and  $d^2$  rhenium oxo complexes, the lowest energy transition is  $d_{xy} \rightarrow (d_{xz}, d_{yz})$ , the latter orbitals being antibonding with respect to the metal–oxo  $\pi$  bonds. However, the situation is different for benzyldiyne complexes: the investigations by Hopkins et al.<sup>18</sup> on  $d^1$   $\text{W}(\text{V})$  species and by Schanze, McElwee-White, and co-workers<sup>20</sup> on  $d^2$   $\text{Mo}(\text{IV})$  and  $\text{W}(\text{IV})$  analogues suggested that there is

significant mixing between the  $(d_{xz}, d_{yz})$  orbitals and benzyldiyne ligand. They denoted the LUMO to be  $\pi^*(\text{M}\equiv\text{C}-\text{Ar})$ , derived from the out-of-phase combination  $d_{xz}(\text{M})-p_x(\text{C})$  or  $d_{yz}(\text{M})-p_y(\text{C})$ . Thus, by comparison to previous studies,<sup>6,8,18</sup> we tentatively assign the lowest energy bands in **2** and **3** to the spin-allowed  $d_{xy} \rightarrow [\pi^*(\text{Re}\equiv\text{C}-\text{Ar})]$  transition (we suggest that this transition contains  $d-d$  character and is not purely MLCT). The halide-to-metal charge-transfer contribution in these transitions is minor in view of the small energy difference between **2** and **3**.

Excitation of **2** (Figure 3b) and **3** in  $\text{CH}_2\text{Cl}_2$  at 658 and 696 nm, respectively, gives red emission (Table 2). The same emission spectra are obtained upon excitation at 300–400 nm. The minor energy difference between the lowest energy absorption band and the emission implies that this excited state also originates from the  $d_{xy} \rightarrow [\pi^*(\text{Re}\equiv\text{C}-\text{Ar})]$  transition. The classification of this excited state as metal-centered ( $d-d$ ) or MLCT depends on the relative rhenium and carbon parentage in the  $\pi^*(\text{Re}\equiv\text{C}-\text{Ar})$  orbital, and this is not resolved in the present study. However, the small shift in emission energy between **2** and **3** suggests that there is little halide-to-rhenium-(VI) LMCT character in the excited state.

Cyclic voltammetry experiments on **2** in dichloromethane show irreversible reduction and oxidation waves at  $-1.48(2)$  and  $1.02(2) \text{ V}$  vs  $\text{Ag}/\text{AgNO}_3$ , respectively. Corresponding waves for **3** appear at  $-1.59(2)$  and  $0.65(2) \text{ V}$  vs  $\text{Ag}/\text{AgNO}_3$ . Fluorescent oxomolybdenum(V) complexes are known to undergo photoinduced electron-transfer reactions.<sup>6</sup> In this work, we find that the emission lifetimes of **2** and **3** (0.49 and 0.41  $\mu\text{s}$ , respectively) are sufficient for viable photoredox processes. For example, the emission of **2** is quenched by  $N,N'$ -dimethyl-4,4'-bipyridinium hexafluorophosphate in  $N,N$ -dimethylformamide solution with a rate constant of  $9.2(2) \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ .

In summary, reports of emissive alkylidyne complexes are confined to  $d^2$  metal centers, e.g.,  $\text{Mo}(\text{IV})$  and  $\text{W}(\text{IV})$ ,<sup>14d,20,21</sup>  $\text{Re}(\text{V})$ ,<sup>10</sup> and  $\text{Os}(\text{VI})$ .<sup>22</sup> This study demonstrates that  $d^1$  congeners also exhibit attractive photochemical properties.

**Acknowledgment.** We thank Prof. X. Z. You (Nanjing University, P.R. China) for magnetic moment measurements, Mr. F. Xue (The Chinese University of Hong Kong) for X-ray crystal structure determination, and The University of Hong Kong, Croucher Foundation and Hong Kong Research Grants Council for financial support.

**Supporting Information Available:** Tables giving crystal data, atomic coordinates, calculated hydrogen coordinates, anisotropic displacement coefficients, and bond distances and angles for **2** (8 pages). Ordering information is given on any current masthead page.

IC970342E

- (20) Schoch, T. K.; Main, A. D.; Burton, R. D.; Lucia, L. A.; Robinson, E. A.; Schanze, K. S.; McElwee-White, L. *Inorg. Chem.* **1996**, *35*, 7769.  
 (21) Bocarsly, A. B.; Cameron, R. E.; Rubin, H. D.; McDermott, G. A.; Wolff, C. R.; Mayr, A. *Inorg. Chem.* **1985**, *24*, 3976.  
 (22) Trammell, S.; Sullivan, B. P.; Hodges, L. M.; Harman, W. D.; Smith, S. R.; Thorp, H. H. *Inorg. Chem.* **1995**, *34*, 2791.