Air-stable fluorescent primary phosphine complexes of molybdenum and tungsten

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ABSTRACT
Here we report a study on the reactivity of the fluorescent air-stable primary phosphine 8-((4-phosphino)phenyl)-4,4-dimethyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene 4 with [Mo(CO)₆], [W(CO)₆], [Mo(CO)₄(piperidine)] and [W(CO)₄(piperidine)] which yields the monophosphine [Mo(CO)₅(4)]₅, [W(CO)₅(4)]₆ and di-phosphine cis-[Mo(CO)₄(4)₂]₇ and cis-[W(CO)₄(4)₂]₈ complexes as the predominant products. In addition to the characterization of these complexes by multinuclear NMR and IR spectroscopy, and mass spectrometry, the solid-state structures of 6 and cis-7 have also been determined by single-crystal X-ray diffraction. The photophysical properties of the complexes show that the incorporation of the phosphorus ligand has a limited effect on the absorption and emission profile of the Bodipy core and that they retain similar quantum yields to their parent Bodipy dyes. Small quantities of the by-products trans-[Mo(CO)₄(4)₂] trans-7, cis-[Mo(CO)₄(piperidine)(4)] cis-8 and cis-[W(CO)₄(piperidine)(4)] cis-10 were also isolated and characterized.

1. Introduction
Primary phosphines are widely regarded as difficult to handle and have a reputation for toxicity, volatility and spontaneous inflammability [1]. Their use has therefore been somewhat limited despite the fact they are versatile starting materials with two reactive P–H bonds. Primary phosphines and their derivatives have found applications in medicinal chemistry [2], polymer science [3], carbohydrate functionalization [4], macrocycle synthesis [5] and catalysis [6]. However, we have recently developed a working model based on Density Functional Theory which indicates that contrary to popular belief, many primary phosphines will be air-stable if the molecule contains the appropriate degree of π-conjugation or heteroatoms – a stabilizing feature quite separate from the known phenomenon of steric hindrance [7]. This model helped us to rationalize our preparation of the first air-stable chiral primary phosphines [8] and
predicted that incorporation of the phosphino group onto the highly conjugated boron dipyrromethene (Bodipy) skeleton would result in a similar resistance to air oxidation. We have since prepared the first air-stable fluorescent primary phosphines [9], and used them to synthesize tridentate tertiary phosphine ligands that complex rhenium and technetium, which we have then exploited in biological cell imaging [10]. Despite the extensive coordination studies of tertiary phosphines to transition metals, the corresponding studies of primary phosphines remains relatively scarce [11], and the coordination of fluorescent primary phosphines has not yet been reported, not withstanding a short preliminary report by ourselves [12]. Of particular interest to us are the group 6 metal complexes, which are routinely prepared with tertiary phosphines to gain a greater understanding of their electronic properties [13]. Here, we report molybdenum and tungsten complexes of the most fluorescent primary phosphine we have prepared to date, and describe their somewhat surprising photophysical properties.

2. Experimental

2.1. General procedure

All air- and/or water-sensitive reactions were performed under a nitrogen atmosphere using standard Schlenk line techniques. Tetrahydrofuran and toluene were dried over sodium/benzophenone and sodium, respectively, and dichloromethane was dried over calcium hydride – these solvents were distilled prior to use. Solvents used for column chromatography were not anhydrous. All starting materials were purchased from Aldrich, Acros Organics, Alfa Aesar, or Strem and used as received. The primary phosphine 8-((4-phosphino)phenyl)-4,4-dimethyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene [14], cis-[Mo(CO)$_4$(pip)$_2$] [13(a)] and cis-[W(CO)$_4$(pip)$_2$] [15] were prepared according to literature procedures. Flash chromatography was performed on silica gel from Fluorochem (silica gel, 40–63 μ, 60 A). Thin-layer chromatography was carried out on Fisher aluminum-based plates with silica gel and fluorescent indicator (254 nm). 1H, 13C{1H}, 31P{1H}, 31P-1H, and 11B{1H} NMR spectra were recorded on a JeOL Lambda 500 (1H 500.16 MHz), JeOL eCS-400 (1H 399.78 MHz), or Bruker avance III 300 (1H 300.13 Hz) spectrometer at room temperature (21 °C); 1H and 13C shifts are reported relative to tetramethylsilane, 31P relative to 80% H$_3$PO$_4$ and 11B relative to BF$_3$.et$_2$O. Infrared spectra were recorded on a varian 800 FT-IR spectrometer and mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Center, Swansea.

2.2. Synthesis of the mono-substituted complexes

2.2.1. [Mo(CO)$_5$(4)]

A solution of [Mo(CO)$_6$] (0.066 g, 0.25 mmol) in anhydrous THF (15 mL) was irradiated with UV light in a quartz vessel under a stream of nitrogen at room temperature for 1 h. Primary phosphine 4 (0.100 g, 0.25 mmol) in anhydrous THF (15 mL) was added and the mixture was irradiated for a further 2 h. The solvent was removed and the red product was purified by column chromatography (hexane:chloroform, 4:1), to yield the intended product as an orange solid (0.041 g, 25.6%). 1H NMR (300 MHz, CDCl$_3$) δ 7.66 (m, 2H), 7.42 (m, 2H), 5.56 (d, $J_{HP} = 326.7$ Hz, 2H), 2.45 (s, 6H), 2.31 (q, $J = 7.5$ Hz, 4H), 1.25 (s, 6H), 0.99 (t, $J = 7.5$ Hz, 6H), 0.28 (s, 6H) ppm; 13C{1H} NMR (75 MHz, CDCl$_3$) δ 208.8 (d, $J_{CP} = 24.2$ Hz), 204.7 (d, $J_{CP} = 9.8$ Hz), 151.2, 139.9, 138.7, 133.6, 132.9, 132.7 (d, $J_{CP} = 11.7$ Hz), 130.0 (d, $J_{CP} = 10.6$ Hz), 128.8, 126.8 (d, $J_{CP} = 42.3$ Hz), 17.6, 14.8, 14.5, 12.1, 10.4 (br) ppm; 31P-1H NMR (121 MHz, CDCl$_3$) δ −63.5 (tt, $J_{PH} = 326.7$ Hz, $J_{PH} = 11.8$ Hz) ppm; 11B{1H} NMR (96 MHz, CDCl$_3$) δ −2.2 ppm; IR (neat) $\tilde{\nu} = 2962, 2929, 2868, 2076, 1992, 1929$ cm$^{-1}$; HRMS (APCI$^+$) Calcd. for C$_{30}$H$_{35}$B$_1$N$_2$P$_1$O$_5$Mo$_1$ [M + H]$^+$ requires $m/z$ 636.1476, found 636.1493 (2.7 ppm).

2.2.2. [W(CO)$_5$(4)]

A solution of [W(CO)$_6$] (0.050 g, 0.14 mmol) in anhydrous THF (15 mL) was irradiated with UV light in a quartz vessel under a stream of nitrogen at room temperature for 1 h. Primary phosphine 4 (0.057 g,
0.14 mmol) in anhydrous THF (15 mL) was added and the mixture was irradiated for a further 2 h. The solvent was evaporated and purified by column chromatography (hexane:chloroform, 4:1) which yielded a red solid (0.018 g, 17.6%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.67 (m, 2H), 7.46 (m, 2H), 5.91 (d, $J_{PH}$ = 340.3 Hz, 2H), 2.46 (s, 6H), 2.32 (q, $J_{HH}$ = 7.6 Hz, 4H), 1.25 (s, 6H), 0.99 (t, $J_{HH}$ = 7.6 Hz, 6H), 0.29 (s, 6H) ppm; $^{31}$C($^1$H) NMR (75 MHz, CDCl$_3$) $\delta$ 198.3 (d, $J_{CP}$ = 23.1 Hz), 195.5 (d, $J_{CP}$ = 7.2 Hz), 151.3, 140.2, 138.5, 133.6, 132.9, 132.8 (d, $J_{CP}$ = 11.3 Hz), 130.1 (d, $J_{CP}$ = 10.5 Hz), 128.8, 126.1 (d, $J_{CP}$ = 47.3 Hz), 17.6, 14.8, 14.5, 12.2, 10.5 (br) ppm; $^{31}$P-$^1$H NMR (102 MHz, CDCl$_3$) $\delta$ = $-$1.6 ppm; IR (neat): $\tilde{\nu}$ = 2361, 2340, 2077, 1993, 1951 cm$^{-1}$; HRMS (ESI+) Calcd. for C$_{54}$H$_{69}$B$_2$N$_4$P$_2$O$_4$Mo (M + H)$^+$ requires m/z 1012.4078 (0.6 ppm).

### 2.3. Synthesis of the di-substituted complexes

#### 2.3.1. cis-[Mo(CO)$_4$(pip)$_2$] cis-7

Cis-[Mo(CO)$_4$(pip)$_2$] (0.070 g, 0.19 mmol) and 4 (0.150 g, 0.37 mmol) were dissolved in anhydrous dichloromethane (6 mL) under nitrogen. The reaction was refluxed for 2 h; complete consumption of the starting material was monitored by $^{31}$P NMR spectroscopy. The solvent was evaporated and the complex purified by column chromatography on silica gel (petroleum ether/dichloromethane, 3:1) to yield an orange solid (0.021 g, 10.9%). $^1$H NMR (500 MHz, CDCl$_3$)

#### 2.3.2. Trans-[Mo(CO)$_4$(pip)$_2$] trans-7

The complex was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 3:1) to yield an orange solid (0.120 g, 62.1%). A sample suitable for X-ray crystallographic analysis was obtained from chloroform/pentane. $^1$H NMR (500 MHz, CDCl$_3$)

#### 2.3.3. cis-[Mo(CO)$_4$(pip)4] cis-8

The complex was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 5:1) to yield an orange solid (0.012 g, 9.1%). $^1$H NMR (500 MHz, CDCl$_3$)

#### 2.3.4. cis-[W(CO)$_4$(pip)$_2$] cis-9

Cis-[W(CO)$_4$(pip)$_2$] (0.057 g, 0.12 mmol) and 4 (0.100 g, 0.25 mmol) were dissolved in anhydrous toluene (5 mL) under nitrogen and the reaction was heated to 75 °C for 20 h. The solvent was evaporated and the complex was purified by column chromatography on silica gel (petroleum ether/dichloromethane,
5 : 1) to yield an orange solid (0.092 g, 67.7%). $^{1}H$ NMR (400 MHz, CDCl$_3$) δ 7.64 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HP}$ = 11.8 Hz, 4H), 7.42 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HP}$ = 1.6 Hz, 4H), 5.79 (d, $^{4}J_{HP}$ = 388.9 Hz, 4H), 2.44 (s, 12H), 2.29 (q, $^{3}J_{HH}$ = 7.6 Hz, 8H), 1.24 (s, 12H), 0.96 (t, $^{3}J_{HH}$ = 7.6 Hz, 12H), 0.26 (s, 12H) ppm; $^{13}C$ NMR (100 MHz, CDCl$_3$) δ 203.5 (br dd, CO), 199.3 (pseudo t, $^{2}J_{CP}$ = 7.3 Hz, CO), 151.2, 139.7, 138.6, 133.4, 132.9 (pseudo t, $^{J_{CP}}$ = 5.7 Hz), 132.7, 129.8 (pseudo t, $J_{CP}$ = 4.3 Hz), 128.7, 126.9, 17.4, 14.7, 14.3, 12.0, 10.4 (br) ppm; $^{31}P$-1H NMR (202 MHz, CDCl$_3$) δ −76.9 (t, $^{1}J_{HP}$ = 388.9 Hz, $^{1}J_{PW}$ = 217.4 Hz) ppm; $^{11}B$-1H NMR (128 MHz, CDCl$_3$) δ −2.0 ppm; IR (neat): $\tilde{\nu}$ = 2961, 2926, 2870, 2359, 2341, 2026, 1940, 1912, 1888 cm$^{-1}$; HRMS (eSI+) Calcd. for C$_{54}$H$_{68}$B$_2$N$_4$P$_2$O$_4$W$_1$ [M$^+$] requires m/z 1102.4507, found m/z 1102.4486 (1.9 ppm).

2.3.5. Cis-[W(CO)$_4$(pip)(4)] cis-10

The complex was purified by column chromatography on silica gel (petroleum ether / dichloromethane, 5 : 1) to yield an orange solid (0.008 g, 8.3%). $^{1}H$ NMR (400 MHz, CDCl$_3$) δ 7.65 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HP}$ = 12.5 Hz, 2H), 7.44 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HP}$ = 2.2 Hz, 2H), 5.89 (d, $^{4}J_{HP}$ = 340.8 Hz, 2H), 2.44 (s, 6H), 2.30 (q, $^{3}J_{HH}$ = 7.5 Hz, 4H), 1.55 (s, 6H), 1.24 (m, 11H), 0.97 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H), 0.26 (s, 12H) ppm; $^{31}P$ NMR (202 MHz, CDCl$_3$) δ −85.0 (tt, $^{1}J_{PH}$ = 340.8 Hz, $^{3}J_{PH}$ = 12.0 Hz, $^{1}J_{PW}$ = 223.2 Hz) ppm; $^{11}B$ NMR (128 MHz, CDCl$_3$) δ −1.9 ppm; IR (neat): $\tilde{\nu}$ = 2954, 2921, 2852, 2361, 2332, 2024, 1986, 1942, 1924 cm$^{-1}$; HRMS (ESI$^+$) Calcd. for C$_{34}$H$_{45}$B$_1$N$_3$P$_1$O$_4$W$_1$ [M$^+$] requires m/z 783.2838, found m/z 783.2842 (0.5 ppm).

2.4. Absorption and emission spectroscopy

Absorption spectra were recorded on a Hitachi Model U-3310 spectrophotometer while fluorescence studies were measured using a Hitachi F-4500 fluorescence spectrophotometer. Solvents used for spectroscopic experiments were spectrophotometric grade. Absorption and emission spectra for all compounds were recorded in dry degassed tetrahydrofuran solution at room temperature. Fluorescence quantum yields were measured with respect to 4,4-difluoro-8-phenyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (Φ$F$ = 0.76, $\lambda_{abs}$ = 524 nm, $\lambda_{em}$ = 537 nm, ε = 86,000 M$^{-1}$ cm$^{-1}$, tetrahydrofuran) [6]. Dyes were excited at 485 nm and excitation and emission slits were both set to 5 nm [16].

2.5. Crystallographic studies

Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer, using MoK$_{α}$ radiation ($\lambda$ = 0.71073 Å) for 6 and CuK$_{α}$ radiation ($\lambda$ = 1.54178 Å) for cis-7. Crystal data and refinement details are listed in table 1. Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected for absorption using a multifaceted crystal model for 6 [17] and using a semi-empirical method based on symmetry-equivalent and repeated reflections for cis-7. The structures were solved by direct methods and refined on $F^2$ values for all unique data. All non-hydrogen atoms were refined anisotropically. Hydrogens attached to carbon were positioned with idealized geometry and the thermal parameters constrained using the riding model with U(H) set at 1.2 times Ueq for the parent atom. The positions of H atoms attached to heteroatoms (in this case P) were located using peaks in the Fourier difference map and the thermal parameters constrained using the riding model with U(H) set at 1.5 times Ueq for the parent atom. Oxford Diffraction CrysalisPro was used for data collection and processing [18], and Olex2 [19] using SHELXL [20] for structure solution and refinement. Crystal Impact Diamond was used to generate all other molecular graphics with displacement ellipsoids drawn at the 50% probability level.

3. Results and discussion

3.1. Synthesis of the fluorescent primary phosphine 4

The fluorescent primary phosphine 8-((4-phosphino)phenyl)-4,4-dimethyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene 4 (scheme 1) is a derivative of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene.
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F-Bodipy, which is recognized as being one of the most versatile fluorophores available due to its highly desirable properties: (i) a strong UV absorption profile, (ii) a sharp fluorescence emission peak, (iii) high quantum yields, (iv) high thermal and photochemical stability, (v) negligible triplet state formation, and (vi) good solubility and chemical robustness [21].

The arylbromide 1 was prepared in a one-pot condensation reaction between 3-ethyl-2,4-dimethyl-1-pyrrole, and 4-bromobenzaldehyde. A subsequent palladium-catalyzed coupling reaction with diethylphosphite yielded the fluorescent phosphonate 2. Because the two fluorines do not survive the later reduction step [22], we treated 2 with two equivalents of methyl magnesium bromide to give 3. This was reduced to 4 using lithium aluminum hydride and chlorotrimethylsilane as a dual reducing agent (scheme 1).

As predicted theoretically [23], the experimental $^{31}$P-$^1$H NMR spectra showed no oxidation of 4 in $d$-chloroform solution or in the solid state over seven days in air. The $^{31}$P-$^1$H NMR chemical shift of $\delta = 121.7$ ppm ($J_{PH} = 202.5$ Hz) for 4 is typical for primary phosphines [1, 11]. Phosphine 4 can also be purified by column chromatography on silica gel in air, which is remarkable for this class of compound, and further demonstrates its air stability. Although the details of our DFT model are discussed elsewhere [23], it proposes that incorporation of the phosphino group onto the highly conjugated boron dipyrromethene (Bodipy) skeleton will induce air stability, as is found experimentally. Whilst increasing

### Table 1. Crystallographic data and refinement details for 6 and cis-7.

| Compound | Chemical formula | Formula weight | Temperature | Radiation, wavelength | Crystal system, space group | Unit cell parameters | Cell volume | Z | Calculated density | Absorption coefficient $\mu$ | $F(0 0 0)$ | Crystal color and size | Data collection method | $\theta$ range for data collection | Index ranges | Reflections collected | Independent reflections | Reflections with $F^2 > 2\sigma$ | Min. and max. transmission | Data/restraints/parameters | min. and max. transmission | Goodness-of-fit on $F^2$ | Largest diff. peak and hole |
|----------|----------------|---------------|-------------|-----------------------|-----------------------------|----------------------|-------------|---|-------------------|-----------------------------|----------------|---------------------|-------------------------|-----------------|---------------------|--------------------------|-----------------|---------------------|--------------------------|-----------------|---------------------|
| 6        | $[\text{W(CO)}_5(\text{4}), \text{6}]$ | C$_{39}$H$_{34}$B$_2$N$_2$O$_5$P$_1$W$_1$ | 728.22      | 150.0(2) K           | Monoclinic, P2$_1$ / c     | $a = 11.9768(14)$ Å      | 6053.75(13) Å$^3$ | 8  | 1.598 g cm$^{-3}$ | 3.910 mm$^{-1}$      | 2896           | Orange, 0.21 x 0.11 x 0.04 mm$^3$ | Xcalibur, Atlas, Gemini ultra | 3.4–27.5$^\circ$ | $h = -15$ to $15$, $k = -21$ to $22$, $l = -37$ to $37$ | 92,956 | 13,134 ($R_{int} = 0.0636$) | 0.063 and 0.855 | 13,143/8/773 | 0.603 and 0.855 | 1.041 | 0.55 and $-0.68$ e Å$^{-3}$ | 2.14 and $-1.10$ e Å$^{-3}$ |
| 7        | $[\text{Mo(CO)}_5(\text{4}), \text{cis-7}]$ | C$_{44}$H$_{38}$B$_2$N$_2$O$_5$P$_2$ | 1016.62     | 150.0(2) K           | Triclinic, P1              | $a = 10.6543(8)$ Å, $\alpha = 87.606(6)^\circ$ | 6253.7(4) Å$^3$ | 2  | 1.272 g cm$^{-3}$ | 2.958 mm$^{-1}$      | 1068           | Red, 0.15 x 0.10 x 0.10 mm$^3$ | Xcalibur, Atlas, Gemini ultra | 2.8–62.8$^\circ$ | $h = -12$, $-10$, $k = -18$, $-19$, $-18$, $l = -19$ to $18$ | 15,468 | 8145 ($R_{int} = 0.0399$) | 0.736 and 0.744 | 8145/617/643 | 0.736 and 0.744 | 1.034 | 2.14 and $-1.10$ e Å$^{-3}$ | 2.14 and $-1.10$ e Å$^{-3}$ |

### Scheme 1. The synthetic procedure for the synthesis of the fluorescent bodipy primary phosphine 4.
the \(\pi\)-conjugation in a molecule increases the HOMO energy, this correlates with increasing air stability in the systems we have investigated. Although this may seem counter-intuitive, recent evidence suggests that the mechanism of phosphine air oxidation is via reaction of their radical cations with molecular oxygen [23, 24]. From this perspective, we can rationalize that a radical cation generated from a primary phosphine which contains no or little \(\pi\)-conjugation or heteroatoms (e.g. \(\text{PMe}_3\), \(\text{PET}_3\)) will be a highly reactive species, being generated from a more stable HOMO orbital, and it is plausible that species such as these enter an irreversible oxidative chain reaction with aerobic oxygen. For the primary phosphines with significant unsaturation/heteroatom presence, their radical cations are less reactive. In our calculations, there appears to be an approximate radical cation SOMO energy threshold of −10 eV; phosphines (not just primary phosphines) whose SOMO values are above this value have so far been found to be air-stable. Note that 4 has a calculated SOMO energy of −8.94 eV [12].

### 3.2. Molybdenum and tungsten carbonyl complexes of the fluorescent primary phosphine 4

In order to ascertain whether the air stability of 4 affects its ability to coordinate to transition metals, and also to establish the effect of any complexation on its photophysical properties, 4 was reacted with molybdenum and tungsten. Molybdenum carbonyl complexes of phosphines are often synthesized in order to gain an insight into the electronic nature of the phosphine, as the complexes give characteristic IR absorptions in the carbonyl region dependent upon the substituents on the phosphorus; better electron donors/poorer acceptors give rise to lower carbonyl stretching frequencies. \(\text{Cis-}[\text{Mo(CO)}_4(\text{PR}_3)_2]\) complexes give \(\text{A}\) carbonyl stretching frequencies that correlate linearly with those found in the extensively studied \(\text{[Ni(CO)}_3(\text{PR}_3)]\) series of compounds [25], evading the need to use the highly toxic \(\text{[Ni(CO)}_4]\) precursor and are thus particularly attractive [26]. \(\text{[W(CO)}_5(\text{PR}_3)]\) complexes have also been prepared and their \(^{31}\text{P}\) \(^{183}\text{W}\) NMR coupling constants have been shown to increase linearly with the stretching frequencies of the carbonyl E mode [27], and although this correlation was found to be weak for a different series of complexes prepared by Keiter and Verkade [28], they did establish a linear relationship between higher values of coupling constant and a greater electronegativity of the substituents on the phosphorus donor, which was discussed further by McFarlane et al. [29]. In addition, tungsten carbonyl complexes have been used to stabilize alkyl primary phosphines that have not been observed in the free state [11(b), 30] and primary alkynyl and allenylphosphines that are otherwise highly unstable [11(b), 31]. Mathey has shown that \(\text{[W(CO)}_5(\text{RPH}_2)]\) forms when 7-phosphanorbornadiene complexes of tungsten pentacarbonyl are reacted with dihydrogen under 20 bar pressure at 150 °C [32], and also that primary mono-phosphine complexes of both tungsten and molybdenum can be used to prepare metal-bound Phospha-Wittig reagents that react further to give phosphaalkenes [33]. Furthermore, \(\text{[M(CO)}_5(\text{RPH}_2)]\) complexes of both tungsten and molybdenum react with 1,2-diethynylbenzene to give complexed benzophosphepins which can be used to generate reactive metal-bound phosphinidenes [34]. For these reasons, we thought it would be interesting to synthesize both the mono-substituted \(\text{[M(CO)}_5(4)]\) and di-substituted \(\text{[M(CO)}_4(4)_2]\) family of complexes (\(M = \text{molybdenum, tungsten}\)), and to study their structural and spectroscopic properties (scheme 2). Thus, 4 was reacted with \([\text{Mo(CO)}_6]\)
and [W(CO)₆] in THF under UV irradiation, which led to the mono-substituted complexes [Mo(CO)₅(4)] and [W(CO)₆(4)] 6, respectively. A d-chloroform solution of 5 gave a downfield peak relative to 4 in the 3¹P NMR spectrum at δ −63.5 ppm, with a 1JP coupling constant of 326.7 Hz, which compares well with the related [Mo(CO)₅(FeCH₂CH₂PH₂)] complex reported by Henderson (Fc = ferrocene; δ −63.2 ppm, 1JP = 315 Hz) [13(b)]. The [Mo(CO)₅(FeCH₂CH₂PH₂)] derivative recently published by Hey-Hawkins and co-workers [35] gave a comparable 1JP coupling constant of 328.0 Hz. The 13C NMR spectrum of 5 showed a doublet splitting of 24.2 Hz on the resonance at δ 204.7 ppm, which is attributable to the carbonyl trans to the phosphine ligand, by virtue of the larger 2JC coupling [35–37]. The equatorial carbonyls gave a peak at δ 204.7 ppm (2JC = 9.8 Hz), the lower chemical shift consistent with those for related complexes (table 2). The IR spectrum of 5 gave three carbonyl stretching vibrations at 2076 (a₁, trans/cis) and 1929 (E) cm⁻¹ in accordance with the C₄ᵥ point group [36–38]. The analogous tungsten complex [W(CO)₅(4)] 6 in d-chloroform gave a 3¹P NMR spectrum which showed a peak at δ −85.7 ppm with a 1JP coupling constant of 340.6 Hz, and 1³¹W satellite peaks that are separated by a 1JP coupling constant of 222.9 Hz. The related complex [W(CO)₅(PhPH₂)] gave corresponding values of δ −90.2 ppm, 1JP of 343.5 Hz and 1JP of 220 Hz in d₄-benzene [29]. The axial carbonyl of 6 gave a peak in the 1³¹C NMR spectrum at δ 198.3 ppm (2JC = 23.1 Hz) and the equatorial carbons gave a peak at 195.5 ppm (2JC = 7.2 Hz), both resonances upfield to that of the molybdenum complex 5, a trend again consistent with the complexes in table 2 and [Mo(CO)₅(PMe₃)] and [W(CO)₅(PMe₃)]. For the tertiary phosphine complexes this pattern has been discussed in terms of the n-donor strength of the metal within its triad [36]. The IR values are consistent with the formula given for 6, with carbonyl bands recorded at 2077, 1973, and 1902 cm⁻¹, the (generally) lower wavenumbers relative to the molybdenum analog 5 are again consistent with similar comparisons of the group 6 primary phosphine complexes (table 2) and for the tertiary phosphine complexes [Mo(CO)₅(PMe₃)] and [W(CO)₅(PMe₃)] [36]. This is in accord with the findings of Gilroy et al, who noted that for their series of ferrocenyl-based [M(CO)₅(RPH₂)] complexes the extent of π-backbonding based on the values of the a₁ carbonyl stretching frequencies increases from molybdenum to tungsten, following trends in metal electronegativity [38]. A cry stalline sample of 6 was analyzed by X-ray crystallography and the solid-state structure determined (figure 1). The bond lengths and angles (figure 1) were found to be comparable with those in the related [W(CO)₅(FeCH₂CH₂PH₂)] [38].

During our studies into air-stable chiral primary phosphines [8], we successfully prepared cis-[Mo(CO)₅(RPH₂)] 1 by following Henderson and Alley's method of reacting two equivalents of FeCH₂CH₂PH₂ with [Mo(CO)₅(pip)] (Fc = ferrocene, pip = pipеридине) [13(c)]. Therefore, 4 was reacted with cis-[Mo(CO)₅(pip)] 2 in refluxing dichloromethane to form the di-substituted product cis-[Mo(CO)₅(4)] 6.

Table 2. Selected NMR and IR spectroscopic data for [M(CO)₅(RPH₂)].

| Complex | ν(CO) | δ¹P PH | δ¹P CO | ν(CO) | δ¹P PH | δ¹P CO | CP coupling |
|---------|------|------|------|------|------|------|------------|
| [Mo(CO)₅(4)] 5³ | 2076 | 1992 | 1929 | 63.5 | 326.7 | – | 208.8 (9.8) |
| [W(CO)₅(4)] 6⁴ | 2077 | 1973 | 1902 | 85.7 | 340.6 | 222.9 | 193.8 (23.1) |
| [W(CO)₅(PhPH₂)] 5⁵ | 2074 | 1950 | 1933 | 81.5 | 328.0 | – | 208.8 (23.7) |
| [Mo(CO)₅(1-AdPH₂)] 8 | 2073 | 1935 | 1916 | 101.8 | 341.5 | 221 | 191.8 (22.2) |
| [W(CO)₅(1-AdPH₂)] 9 | 2073 | 1968 | 1926 | 103.1 | 347 | 216 | 196.2 (7) |
| [W(CO)₅(1-AdPH₂)] 10 | 2074 | 1987 | 1952 | 28.5 | 308.18 | – | 208.34 (21.99) |

³IR recorded neat, NMR in d₄-chloroform.
⁴NMR in d₄-benzene [29].
⁵IR in petroleum spirit, NMR in d₄-chloroform [13(b)].
⁶IR in nujol, NMR in d₄-chloroform [35].
⁷IR in THF, NMR in d₄-THF [39].
cis-7 (scheme 2). Coordination of the phosphine to the molybdenum resulted in a downfield shift of the $^{31}$P{1H} NMR signal from $\delta -121.7$ ppm for the free phosphine to $\delta -56.1$ ppm for the complex, as expected, and an increased $^1J_{PH}$ coupling was observed from 202.5 Hz for 4 to 318.9 Hz for complex cis-7. The carbonyl region of the $^{13}$C NMR spectrum gave a pseudo-triplet at 207.8 ppm with a splitting of $^2J_{CP}$ of 9.4 Hz which is assigned to the carbonyls cis to the primary phosphines. The furthest downfield peak at $\delta 213.1$ ppm appears as a broad doublet of doublets and is attributable to the two carbonyls trans to the phosphine ligands. This is consistent with the assignment of the carbonyls in cis-[Mo(CO)$_4$(FcPH$_2$)$_2$] [35] and cis-[Mo(CO)$_4$(PhPH$_2$)$_2$] [40]. Similarly, the IR spectrum further supports the structure of 7 as the cis-isomer, showing four distinct bands for the two $A_1$, $B_1$, and $B_2$ stretching frequencies at 2029, 1947, 1919, and 1896 cm$^{-1}$, again comparing well with the aforementioned analogs. The lowered wavenumbers of the $A_1$ carbonyl stretching frequencies in cis-7 is consistent with greater back bonding to those ligands compared to 5, as a result of the introduction of the second phosphine donor. Crystals of cis-7 were grown by slow diffusion (chloroform/pentane) and its solid-state structure is given in figure 1. Typical phosphorus–molybdenum, phosphorus–carbon, and molybdenum–carbon bond lengths, and the phosphorus–molybdenum–carbon bond angles are as expected (figure 1) and compare well with those determined for the related complexes cis-[Mo(CO)$_4$(PhPH$_2$)$_2$] [40], cis-[Mo(CO)$_4$(FcCH$_2$PH)$_2$] [13(b)], cis-[Mo(CO)$_4$(1,2-Fc(CH$_2$PH)$_2$)$_2$] [13(c)], cis-[Mo(CO)$_4$BuN(CH$_2$CH$_2$PH)$_2$] [41] and cis-[Mo(CO)$_4$(Ph$_2$CONH)$_2$] [39]. The carbonyls trans to the phosphine ligands exhibit shorter metal–carbon bond lengths than those trans to another carbonyl, which indicates that the carbonyl ligand has a stronger trans influence than the primary phosphine 4 (the same is also true for the tungsten complex 6). As a minor
product trans-[Mo(CO)₄(4)₂] trans-7 was also observed and isolated by column chromatography in a 10.9% yield. This compound gave a triplet of complex multiplets in the ³¹P-¹H NMR spectrum at δ −48.8 ppm (Jₚₜₚ = 316.5 Hz). Finally cis-[Mo(CO)₄(pip)(4)] cis-8 was also isolated in very small quantities—the ³¹P-¹H NMR spectrum gave a triplet of triplets at δ −63.5 ppm (Jₚₜₚ = 327.7 Hz). In contrast, Henderson et al. showed that the reaction of 1,2-Fc(CH₂PH₂)₂ and cis-[Mo(CO)₄(pip)]₂ in refluxing dichloromethane produced cis-[Mo(CO)₄(1,2-Fc(CH₂PH₂)₂)] as the sole product [13(c)]. Daresbourg et al. investigated the mechanism of tertiary phosphine coordination to cis-[Mo(CO)₄(pip)]₂ and showed cis-[Mo(CO)₄(pip)(PR₃)] species are intermediates in the formation of cis-[Mo(CO)₄(PR₃)₂] [13(a)].

The corresponding reaction of two equivalents of 4 with cis-[W(CO)₄(pip)]₂ in toluene at 75 °C for 20 h led to cis-[W(CO)₄(4)] cis-9 as the major product (scheme 2). Coordination of the phosphine again resulted in a shift of the ³¹P-¹H NMR signal from δ −121.7 ppm for the free phosphine to δ −76.9 ppm for the complex, which showed an increased Jₚₜₚ coupling from 202.5 Hz for the uncoordinated primary phosphine 4 to 388.9 Hz for cis-9. The presence of ¹⁸³W satellites were also visible on the spectrum, which gave a Jₚₜₚ coupling of 217.4 Hz. The ¹³C NMR spectrum showed a pseudo-triplet at δ 199.3 ppm with a splitting of 2Jₚₚ, of 7.3 Hz, which is once again assigned to the carbonyls cis to the primary phosphines. The furthest downfield peak at δ 203.5 ppm appears as a broad doublet of doublets and is attributable to the two carbonyls trans to the phosphine ligands. The carbonyl stretching frequencies in the IR spectrum of cis-9 are lower than those for the molybdenum analog cis-7, a pattern also observed for the mono-phosphine complexes 5 and 6 as discussed earlier, and were recorded at 2026, 1940, 1912, and 1888 cm⁻¹. As was also observed for the molybdenum complexes, the presence of the second phosphine in cis-9 results in lower corresponding a₁ carbonyl stretching frequencies when compared to cis-7, as was also observed for the molybdenum analog cis-[Mo(CO)₄(pip)(4)] as the sole product [13(c)].

**3.3. Photophysical data for 4, 5, 6, cis-7 and cis-9**

Photophysical data were collected in dry, nitrogen-purged tetrahydrofuran (table 3). The absorption profiles of primary phosphine 4 and its predominant molybdenum and tungsten metal-carbonyl complexation products are represented in figure 2; the low-energy maxima (λ_max) for 4 appears at 512 nm and is assigned to the S₀-S₁ (π-π*) electronic transition associated with the Bodipy core. The high molar absorption coefficient (ε, 79,000 M⁻¹ cm⁻¹) is in keeping with previous findings for Bodipy compounds [21]. The broader and less intense band seen at ca 375 nm corresponds to the S₀-S₃ (π-π*) transition of the boradiazaindacene unit. The fluorescence quantum yield (Φ_f) of 0.33 for 4 compares well to the parent bodipy, where the phosphino group is replaced by hydrogen, which has a Φ_f value of 0.35 [9]. This observation was not entirely unexpected given the results from our DFT calculations which showed that phosphorus orbital participation was significant at HOMO-3 for 4 but not at any occupied orbital above [9, 12]. These findings contradict many of the amine examples and the few examples of phosphines conjugated to organic fluorophores [42] in which the fluorescence is quenched, a phenomenon often attributed to reductive-photoinduced electron transfer (PeT). Fluorescence quenching of organic dyes in the presence of heavy metals is well documented due to the normally facile accessibility of the triplet state [43].

The complexes cis-[Mo(CO)₄(4)₂] cis-7 and cis-[W(CO)₄(4)₂] cis-9 also showed typical Bodipy absorption curves [21] with the same absorption maxima as 4 at 512 nm (table 3). The di-substituted metal complexes have much larger molar absorption coefficients in comparison to 5 and 6 due to the presence of two Bodipy ligands, which gives values of ε of 148,000 and 133,000 M⁻¹ cm⁻¹ for cis-7 and cis-9, respectively. Room temperature fluorescence is still detected for the complexes and the quantum yields are very similar to that of the uncoordinated primary phosphine (compare Φₕ = 0.33 for 4 versus 0.31 for both cis-7 and cis-9), and thus, little quenching is observed despite the presence of the heavy metal in this system (figure 2). Having described in the introduction how primary phosphine complexes of...
the group 6 metals are ideal precursors to benzophosphepines, phosphinidenes, and phosphaalkenes, our findings highlight the potential to use the complexes described herein in order to prepare highly fluorescent analogs of these exotic organophosphorus compounds.

4. Conclusion

We have demonstrated that the air stability of the fluorescent ligand 4 does not hinder its reactivity in transition metal coordination chemistry, as it readily forms the mono- and di-substituted group 6 metal carbonyl complexes [Mo(CO)\(_5\)(4)] 5, [W(CO)\(_5\)(4)] 6, cis-[Mo(CO)\(_4\)(4)]\(_2\) cis-7, and cis-[W(CO)\(_4\)(4)]\(_2\) cis-9, whose spectroscopic and crystallographic properties are consistent with those found for related complexes of other primary phosphines. The complexes retain similar photophysical characteristics to the uncomplexed 4 with, somewhat surprisingly, little to moderate quenching observed upon coordination. As discussed earlier, [W(CO)\(_5\)(RPH\(_2\))\(_2\)] and [Mo(CO)\(_5\)(RPH\(_2\))\(_2\)] have been used to prepare benzophosphepines, phosphinidenes, and phosphaalkenes, and therefore 5 and 6 ought to provide a convenient gateway to fluorescent derivatives of each of these ligand classes. The preparation and

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**Table 3.** Photophysical data for 4, 5, 6, cis-7 and cis-9.

|        | \(\lambda_{\text{abs}}\) (nm) | \(\varepsilon\) (M\(^{-1}\) cm\(^{-1}\)) | \(\lambda_{\text{em}}\) (nm) | \(\Phi_F\)\(^a\) |
|-------|-------------------------------|---------------------------------|----------------------------|---------------|
| 4     | 512                           | 79,000                          | 526                       | 0.33          |
| 5 (Mo)| 512                           | 72,000                          | 527                       | 0.25          |
| 6 (W) | 512                           | 73,000                          | 527                       | 0.20          |
| Cis-7 (Mo)| 512 | 148,000                        | 528                       | 0.31          |
| Cis-9 (W) | 512 | 133,000                        | 527                       | 0.31          |

Note: Samples were measured in dry, degassed tetrahydrofuran at room temperature.

\(^a\)Fluorescence quantum yields were measured with respect to 4,4-difluoro-8-phenyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene [16]. Dyes were excited at 485 nm.

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Figure 2. Absorption and emission spectra of primary phosphine 4 and its metal complexes 5, 6, cis-7 and cis-9, recorded in tetrahydrofuran at room temperature.
characterization of \(5\) and \(6\), together with the di-substituted complexes \(cis-7\) and \(cis-9\), has also allowed us to gain an insight into the electronic nature of \(4\) and compare it to non-fluorescent primary phosphine analogs.

**Supplementary material**

\(^1\)H and \(^{13}\)C NMR spectra of \(4\), \(5\), \(6\), \(cis-7\), \(cis-8\), \(cis-9\) and \(cis-10\) are provided in the Supplementary Information together with detailed X-ray crystallographic data for \(6\) and \(cis-7\).

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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