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Reactive Intermediates: A Transient Electrophilic Phosphinidene Caught in the Act

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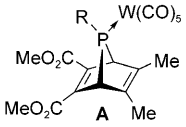
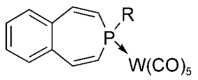
Phosphinidene complexes [$L_nM{=}P{-}R$][1] are fascinating reagents akin to the isoelectronic carbenes [$L_nM{=}CR_2$][2] that have made a stunning impact on the preparative and industrial scale syntheses of small molecules and polymeric materials. It is tempting to extend the relationship for low-valent species that is based on the similar electronegativities of the element phosphorus and the diagonally related carbon to these transition-metal complexes.[3] It has already been established that phosphinidene complexes can be classified as electrophilic (Fischer-type) or nucleophilic (Schrock-type) at phosphorus depending on the nature of the ligands L;[4] electron-withdrawing ligands with strong π-acceptor capacity (e.g., CO) reduce the charge concentration on the phosphorus atom and therefore enhance its electrophilicity, whereas strong σ-donor ligands (e.g., Cp) increase the electron density at phosphorus and thereby increase its nucleophilic properties. Proper characterisation of these complexes assists in understanding their chemical potential.

A growing number of nucleophilic phosphinidene complexes, many of the type [$Cp_2(L)M{=}PR$],[1,5] have already been isolated and characterised by X-ray crystallography, as have cationic ones, like [$Cp^*(CO)_2Fe{=}PN\textit{i}Pr_2$][$AlCl_4$],[6] bearing Cp* and CO ligands. Yet, there is still no direct observation of the electrophilic phosphinidene complex [$R{-}P{=}W(CO)_5$], bearing only CO ligands. This transient, purportedly obtained by thermal expulsion from precursors like 7-phosphanorbornadiene (**A**)[7] and 3*H*-3-benzophosphepine (**B**),[8] has been inferred from trapping reactions,[9] such as concerted [1+2] cycloadditions and insertions into σ-bonds, giving access to diverse organophosphorus compounds.[1,10] Whereas [$R{-}P{=}W(CO)_5$] reportedly has been observed in acetonitrile,[11] phosphinidene complexes are also known to give tight complexes or ylides with this solvent.[12] Hence, while the reactivity studies may be compelling, it has been pointed out that "… in almost every case, it is possible to conceive alternative mechanisms, which do not involve phosphinidenes".[13] The present study aims to remove this uncertainty. We now report on the detection of [$R{-}P{=}W(CO)_5$] using electrospray ionisation tandem mass spectrometry (ESI-MS/MS)[14] and demonstrate that its chemical behaviour in the gas phase is indistinguishable from that observed in the condensed phase.



A



B

Detection of phosphinidenes by mass spectrometry necessitates the presence of a charged group, but one that demonstrably and verifiably has no influence on the chemical behaviour of the reactive phosphorus centre. To accomplish this, we modified benzophosphepine complex **1** by incorporating the cationic substituent NMe_3^+ and examined its properties and reactivity (Scheme 1). The desired trimethylammonium salt **1a** was obtained by methyl triflate treatment of its *p*-*N*,*N*-dimethylaminophenyl analogue (^{31}P NMR: $\delta = -14.8$ ppm; ^{13}C NMR: $\delta = 128.8$ ppm, ^1J(C,P) = 37 Hz, PCH), which was synthesised by double hydrophosphination of the corresponding primary phosphine and 1,2-diethynylbenzene.[8,15] Comparison of the NMR spectroscopic data of **1a** (^{31}P NMR: $\delta = -21.0$ ppm, ^1J-

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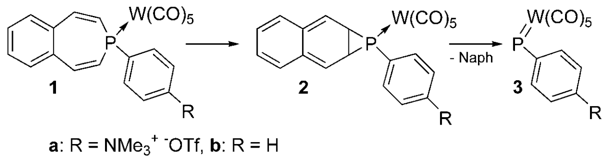


Scheme 1. Fragmentation of 3*H*-benzophosphepines **1**.

(P,W) = 252 Hz; ^{13}C NMR: $\delta = 126.7$ ppm, ^{1}J(C,P) = 37 Hz, P*C*H) with those of benchmark **1b** (R = H; ^{31}P NMR: $\delta = -14.8$ ppm, ^{1}J(P,W) = 238 Hz; ^{13}C NMR: $\delta = 127.6$ ppm, ^{1}J(C,P) = 36 Hz, P*C*H) suggests a minor influence of the cationic label on the electronic properties of the phosphorus atom.

Expulsion of [R–C_6H_4–P=W(CO)$_5$] (**3**) from its precursor **1** appears not to be affected by the cationic label. DFT calculations at B3PW91/6-311+G(d,p) (LANL2DZ for W)[15,16] give virtually identical barriers for the rate-determining rearrangement of charged **1a** and neutral **1b** to phosphanorcaradiene **2** of 27.4 and 26.5 kcal mol^{-1}, respectively (Figure 1). Subsequent fragmentation by [1+2] retro-addition into naphthalene and phosphinidene **3** is exothermic and barrierless[17] for both (**2a**→**3a**: $\Delta E = -4.6$, **2b**→**3b**: −7.7 kcal mol^{-1}). In addition, the HOMO–LUMO gap of the transient phosphinidenes **3** remains unaffected (**3a**: ΔE(HOMO−LUMO) = 2.261 eV, **3b**: 2.259 eV; Figure 1).[18]

To probe whether the cationic label influences the reactivity of benzophosphepine **1**, two benchmark phosphinidene reactions (insertion and addition)[10] were conducted in the condensed phase (Scheme 2). The exclusive methanol O–H bond insertion yielding **4a** (^{31}P NMR: $\delta = 102.7$ ppm, ^{1}J(P,H) = 351 Hz)[19] and the quantitative [1+2] cycloaddition to 1,4-dimethoxy-2-butyne affording solely the three-membered phosphirene **5a** (^{31}P NMR: $\delta = -146.3$ ppm) are similar to those observed for unlabeled **1b**. Thus, assuming that the phosphinidene complex is fully expelled from its precursor, cationic [$Me_3NC_6H_4$–P=W(CO)$_5$]$^+$ (**3a**) and neutral **3b** have comparable reactivities.

Next, we set out to demonstrate the existence of transient electrophilic phosphinidene **3a** as a distinct entity and to examine its chemical reactivity. For this we resorted to gas-phase ion-molecule chemistry using ESI-MS/MS,[14] a methodology that is ideally suited for mechanistic studies providing qualitative guidance to solution-phase reactions. The first step was to bring the precursor ion unperturbed into the gas phase. Introducing a solution of benzophosphepine **1a** in dichloromethane into a Finnigan TSQ Quantum mass spectrometer by means of ESI indeed showed the charged precursor as sole species in good intensity (*m/z*: 618) with an excellent agreement between the observed and calculated isotope patterns (Figure 2 A).[15] When we subjected this ion to collision-induced dissociation (CID) with argon (Figure 2 B) it underwent loss of 128 amu (naphthalene) to generate a species with a mass (*m/z*: 490) and an isotope pattern that is consistent with the formation of [$Me_3NC_6H_4$–P=W(CO)$_5$]$^+$ (**3a**; Scheme 1). The only other dissociation observed was the subsequent loss of CO (e.g., *m/z*: 434 [**3a**−2 CO]; Figure 2 B), which is typical for metal–carbonyl complexes.[20]

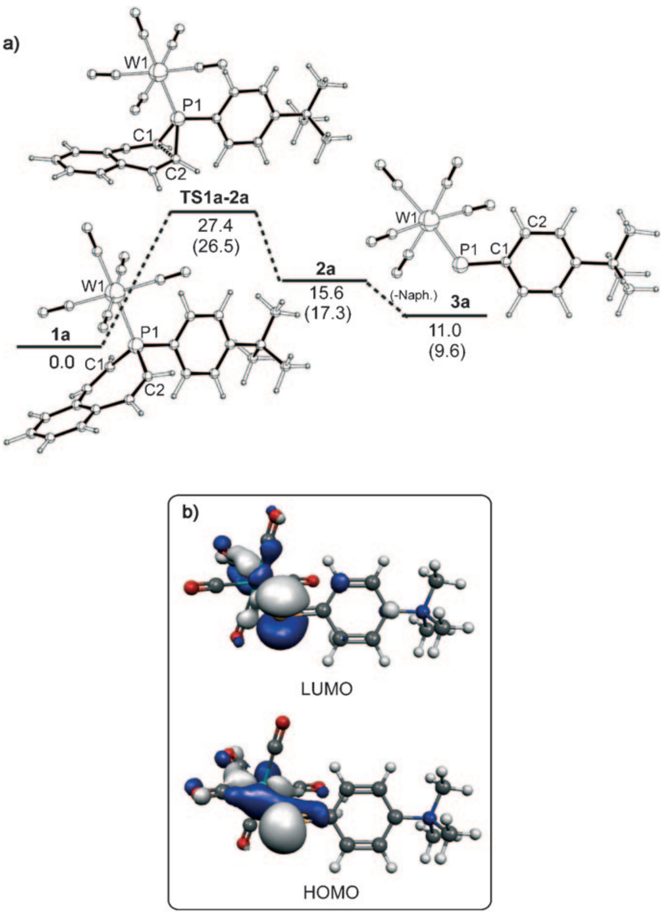
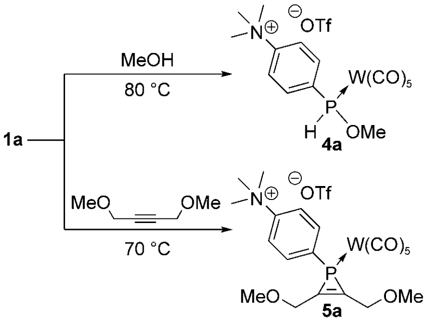


Figure 1. Relative B3PW91/6-311+G(d,p) (LANL2DZ for W) energies (ZPE corrected, in kcal mol^{-1}) for the rearrangement of **1a**,**b** to phosphanorcaradiene **2a**,**b**, and subsequent phosphinidene loss (**3a**,**b**). Selected bond lengths [Å], angles, and torsion angles [°] for **1a** (values for the neutral analogues **b** are given in parentheses): P1–C1,2 1.808 (1.814), C1–C2 2.847 (2.816); **TS1a-2a**: P1–C1,2 1.825 (1.820), C1–C2 1.952 (1.941); **2a**: P1–C1,2 1.915 (1.887), C1–C2 1.512 (1.528); **3a**: P1–C1 1.808 (1.833), P1–W1 2.393 (2.430); C1-P1-W1 113.5 (117.7), C2-C1-P1-W1 49.9 (0.0).



Scheme 2. Insertion and addition reactions of transient phosphinidene [$Me_3NC_6H_4$–P=W(CO)$_5$]$^+$ (**3a**).

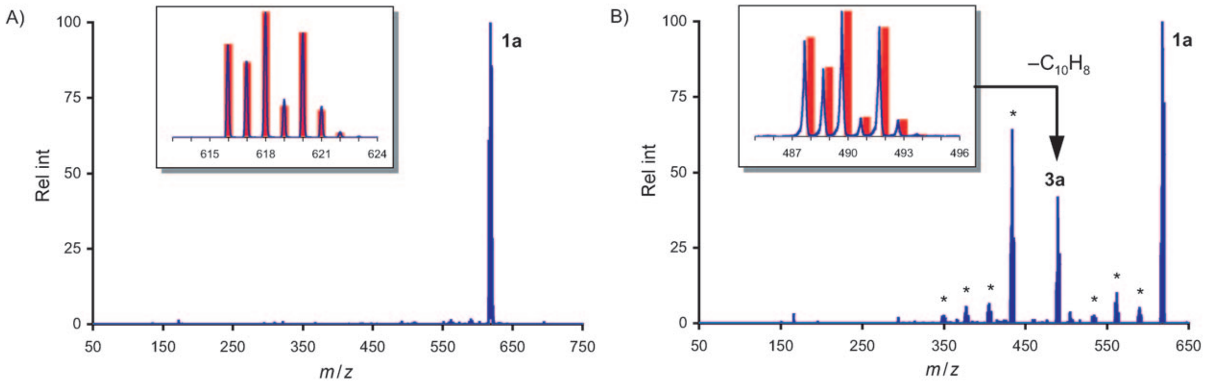


Figure 2. A) ESI MS spectrum of **1a**, and B) spectrum upon collision-induced dissociation with 1.5 mTorr argon at −12 V collision offset. The insets show the calculated (red bars) and experimental isotope patterns of **1a** and **3a**. The signals marked with a * are all dissociation products due to CO loss.

Having detected a mass that corresponds to phosphinidene **3a**,[21] our next move was to probe its reactivity in the gas phase using a modified Finnigan Mat TSQ-700, the original transfer octopole of which was replaced with a long 24-pole ion guide for thermalisation of the ions with a buffer gas.[22] Under proper spraying conditions, benzophosphepine **1a** could again be converted to presumably complex **3a** with CO loss as the only observable side reaction. Upon addition of 10 mTorr of propene as both buffer gas and trapping agent, full conversion to the expected adduct **6a** was observed (m/z: 532; Figure 3 A) indicating that indeed phosphinidene $[Me_3NC_6H_4{-}P{=}W(CO)_5]^+$ (**3a**) had been observed. In a control experiment, **3a** was thermalised with argon buffer gas, mass-selected and then reacted in the collision octopole with 500 µTorr propene to afford the same [1+2] adduct. In this experiment, **6a** was formed at extremely soft collision offset (−3 V), suggesting an effectively barrierless addition, which is in full agreement with the anticipated reactivity of the electrophilic phosphinidene complex.[17] Similar results but with lower efficiencies were ob-

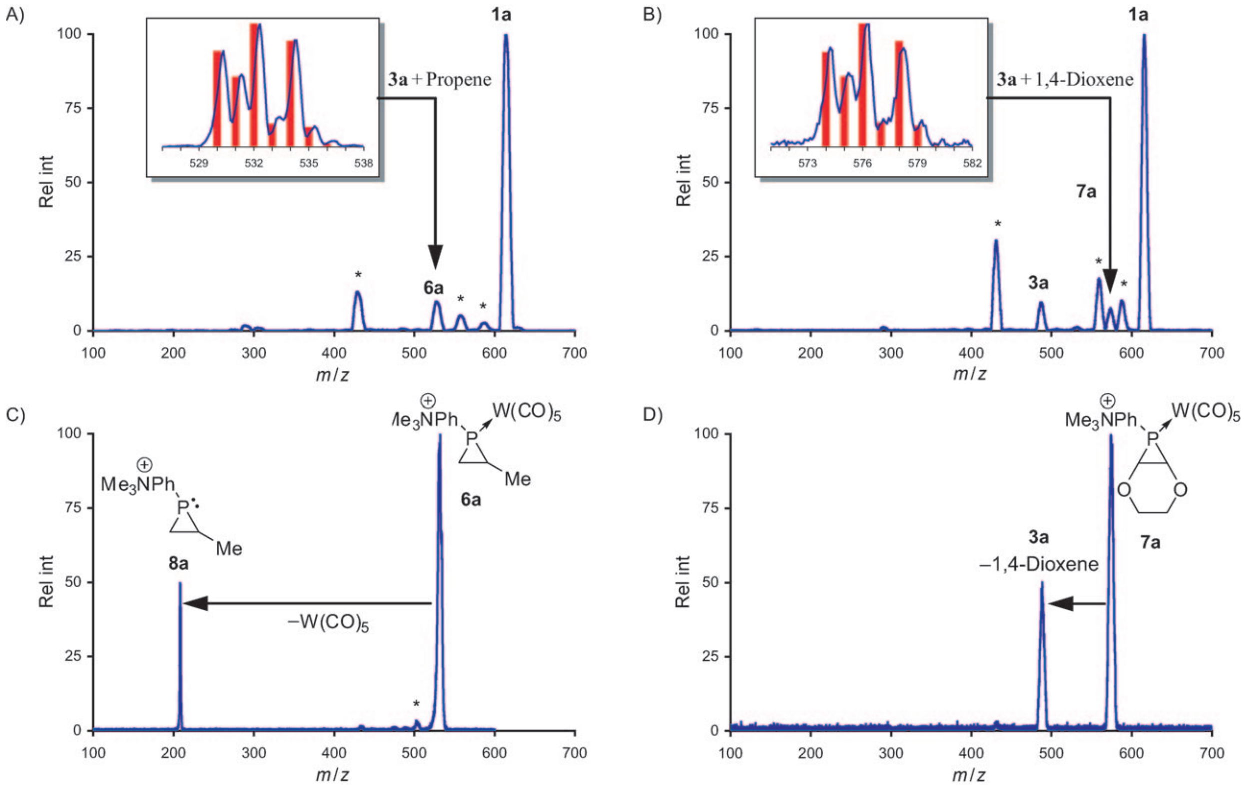


Figure 3. Top: Thermalisation of **3a** with A) 10 mTorr propene, and B) 10 mTorr 1,4-dioxene. The insets show the calculated (red bars) and experimental isotope patterns of adducts **6a** and **7a**. Bottom: Collison-induced dissociation of C) **6a** with 70 µTorr argon at −60 V collision offset, and D) **7a** with 100 µTorr argon at −25 V collision offset. The signals marked with a * are all dissociation products due to CO loss.

tained with ethylene either as buffer or as collision gas (see the Supporting Information), and with 1,4-dioxene to yield phosphirane **7a** (Figure 3B).

The ESI-MS/MS experiments also offer insight into the stability of the three-membered reaction products, which may either undergo decomplexation of the transition-metal group to afford unique phosphirane ligands[23] or serve as precursors to phosphinidenes by [1+2] retroaddition.[24] CID of mass-selected propene adduct **6a** with 70 μTorr argon caused complete loss of the $W(CO)_5$ unit to render metal-free phosphirane **8a** (Figure 3C), thereby simultaneously confirming that **6a** is not a loosely bound ion–molecule complex. On the other hand, CID of bicyclic **7a** with argon gas led exclusively to regeneration of phosphinidene **3a** by elimination of 1,4-dioxene (Figure 3D). These observations are supported by B3PW91/6-311+G(d,p) calculations (LANL2DZ for W)[15,16] that indicate a much higher endothermicity for propene dissociation from **6a** (36.0 kcal mol^{-1}) than liberation of 1,4-dioxene from **7a** (22.0 kcal mol^{-1}), but an equally demanding demetalation of $W(CO)_5$ from the PCC rings (**6a**: $\Delta E = 34.0$, **7a**: 36.4 kcal mol^{-1}). Evidently, the energy required for [1+2] retroaddition is strongly dependent on the ring substituents, just as the metal[25] and phosphorus substituents[24] can influence this process, thereby pointing to new opportunities for the development of efficient phosphinidene precursors.

In summary, the transient electrophilic phosphinidene complex $[R{-}P{=}W(CO)_5]$, carrying a cationic *p*-trimethylammoniumphenyl substituent, was detected by gas-phase mass spectrometric experiments and was shown to give [1+2] cycloadducts with olefins. These observations, supported by density functional calculations and solution-phase benchmarking, give credence to the claimed intermediacy of neutral phosphinidene complexes involved in the synthesis of numerous organophosphorus compounds. The gas-phase studies further illustrate that $W(CO)_5$-complexed PCC-rings can undergo demetalation or [1+2] retroaddition depending on the nature of the phosphirane ring and its substituents, which expands the chemistry of low-valent phosphorus intermediates.

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Keywords: carbenes · cycloaddition · phosphorus · tungsten

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[1] a) J. C. Slootweg, K. Lammertsma in *Science of Synthesis Vol. 42* (Eds.: B. M. Trost, F. Mathey), Thieme, Stuttgart, **2009**, pp. 15–36; b) K. Lammertsma, *Top. Curr. Chem.* **2003**, *229*, 95–119.

[2] a) G. Bertrand, *Carbene Chemistry*, Marcel Dekker, New York, **2002**; b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; c) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[3] K. D. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, New York, **1998**.

[4] A. W. Ehlers, E. J. Baerends, K. Lammertsma, *J. Am. Chem. Soc.* **2002**, *124*, 2831–2838.

[5] a) P. B. Hitchcock, M. F. Lappert, W.-P. Leung, *J. Chem. Soc. Chem. Commun.* **1987**, 1282–1283; b) D. W. Stephan, *Angew. Chem.* **2000**, *112*, 322–338; *Angew. Chem. Int. Ed.* **2000**, *39*, 314–337.

[6] a) B. T. Sterenberg, K. A. Udachin, A. J. Carty, *Organometallics* **2003**, *22*, 3927–3932; b) H. Nakazawa, W. E. Buhro, G. Bertrand, J. A. Gladysz, *Inorg. Chem.* **1984**, *23*, 3431–3433.

[7] a) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485; b) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, 667–668.

[8] a) M. L. G. Borst, R. E. Bulo, C. W. Winkel, D. J. Gibney, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2005**, *127*, 5800–5801; b) M. L. G. Borst, R. E. Bulo, D. J. Gibney, Y. Alem, F. J. J. de Kanter, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2005**, *127*, 16985–16999.

[9] A. Marinetti, C. Charrier, F. Mathey, J. Fischer, *Organometallics* **1985**, *4*, 2134–2138.

[10] a) F. Mathey, N. H. Tran Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938–2957; b) K. Lammertsma, M. J. M. Vlaar, *Eur. J. Org. Chem.* **2002**, 1127–1138.

[11] ^{31}P NMR chemical shifts in acetonitrile at $\delta = 692.9$ (R=Ph) and $\delta = 766.4$ ppm (R=Mes) have been attributed to the free, transient phosphinidene $[R{-}P{=}W(CO)_5]$, see: a) Y. G. Budnikova, T. V. Gryaznova, A. R. Yagfarov, O. G. Sinyashin, *Russ. Chem. Bull.* **2005**, *54*, 1398–1401.

[12] We rather ascribed these signals (ref. [11]) to a base-stabilised phosphinidene, namely P,N-ylide $[(CO)_5W(R)P{-}N{=}CMe]$; see for example: a) R. Streubel, *Top. Curr. Chem.* **2003**, *223*, 91–109; b) A. H. Cowley, R. L. Geerts, C. M. Nunn, *J. Am. Chem. Soc.* **1987**, *109*, 6523–6524; for solvent adducts of nucleophilic phosphinidenes, see: c) H. Aktas, J. Mulder, F. J. J. de Kanter, J. C. Slootweg, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2009**, *131*, 13531–13537.

[13] F. Mathey, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme, Stuttgart, **1990**, p. 34.

[14] a) P. Chen, *Angew. Chem.* **2003**, *115*, 2938; *Angew. Chem. Int. Ed.* **2003**, *42*, 2832—2847; b) A. Fedorov, M.-E. Moret, P. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 8880–8881; c) S. Torker, D. Merki, P. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 4808–4814; d) D. M. Chisholm, J. S. McIndoe, *Dalton Trans.* **2008**, 3933–3945.

[15] See the Supporting Information for details.

[16] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[17] K. Lammertsma, A. W. Ehlers, M. L. McKee, *J. Am. Chem. Soc.* **2003**, *125*, 14750–14759.

[18] The ammonium group lowers both the phosphinidene's highest occupied and lowest unoccupied molecular orbitals (HOMO and

LUMO) that account for the phosphorus lone pair and empty p orbital, respectively. This makes **3a** the more electrophilic species (HOMO **3a**: −8.68, **3b**: −6.17 eV; LUMO **3a**: −6.42, **3b**: −3.91 eV).

[19] The methanol insertion product **5a** shows comparable features to its neutral analogue [W(CO)$_5${PhP(H)OMe}] (^{31}P: $\delta = 105.1$, ^1J(P,H) = 346 Hz), see reference [7a].

[20] See for instance the mass spectrometric experiments in reference [8].

[21] Previously, the aromatic fragment from **A** was detected after thermolysis in a mass spectrometer, suggesting net loss of [Ph−P=M(CO)$_5$] (M = Mo, W); see reference [7b].

[22] The custom-made 24-pole operates similar to the one described in: L. A. Hammad, G. Gerdes, P. Chen, *Organometallics* **2005**, *24*, 1907–1913; details of the new 24-pole design will be reported elsewhere; E. P. A. Couzijn, E. Zocher, A. Bach, P. Chen, unpublished results.

[23] a) A. Marinetti, F. Mathey, L. Ricard, *Organometallics* **1993**, *12*, 1207–1212; b) J. C. Slootweg, M. Schakel, F. J. J. de Kanter, A. W. Ehlers, S. I. Kozhushkov, A. de Meijere, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2004**, *126*, 3050–3051.

[24] The parent W(CO)$_5$-complexed phenylphosphirane undergoes [1+2] retroaddition at 150 °C (3 h), see: A. Marinetti, C. Charrier, F. Mathey, J. Fischer, *Organometallics* **1985**, *4*, 2134–2138, whereas the corresponding diethylamino-substituted phosphirane undergoes [1+2] retroaddition at 70 °C (3 h), see: F. Mercier, B. Deschamps, F. Mathey, *J. Am. Chem. Soc.* **1989**, *111*, 9098–9100.

[25] a) M. L. G. Borst, N. van der Riet, R. H. Lemmens, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, A. M. Mills, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2005**, *11*, 3631–3642; b) J. B. M. Wit, Ph.D. Thesis, Vrije Universiteit (Amsterdam), **2001**.

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