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Preliminary Communication

Phosphine dihalides as reagents for synthesis of tungsten aminomethylidyne complexes

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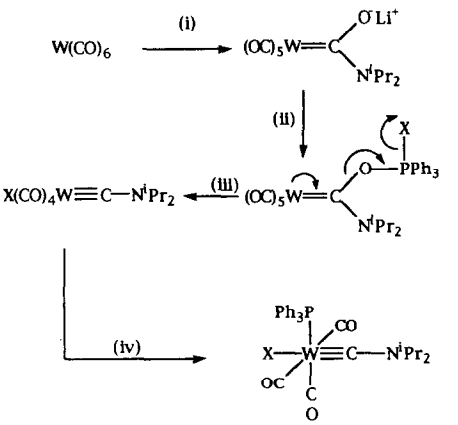
Abstract

Reaction of $[W\{=C(OLi)N^iPr_2\}(CO)_5]$ with X_2PPh_3 and PPh_3 gives the aminomethylidyne complexes mer- $[W(\equiv CN^iPr_2)X(CO)_3(PPh_3)]$ (X = Cl, Br) in a convenient one-pot procedure from $[W(CO)_6]$. The route appears to be general, providing ready access to a range of alkylidyne complexes including $[W(\equiv C\text{-naphthyl})Cl(CO)_2(tmeda)]$, $[W(\equiv C\text{-thienyl})Cl(CO)_2(tmeda)]$, $[W(\equiv C\text{-naphthyl})Cl(CO)_3(PPh_3)]$, $[W(\equiv C\text{-thienyl})Cl(CO)_3(PPh_3)]$ and $[W(\equiv CN^iPr_2)Cl(CO)_2(2,2'\text{-bipyridyl})]$.

The study of aminomethylidyne (2-aza-vinylidene) complexes would be facilitated by simple economic routes to thermally stable but reactive derivatives. We have previously described one such procedure, involving the sequential treatment of $[M(CO)_6]$ (M = Cr, Mo, W) with LiN^iPr_2, $(CF_3CO)_2O$ and PPh_3 to give $[W(\equiv CN^iPr_2)(O_2CCF_3)(CO)_3(PPh_3)]$ [1]. This route has many advantages over the original multi-step method developed by Fischer [2]. We have also encountered some disadvantages. Firstly, trifluoroacetic anhydride is extremely toxic and aged samples are often contaminated with CF_3CO_2H, which leads to a reduction in yields and sometimes makes chromatographic purification necessary. Secondly, if the LiN^iPr_2 is prepared 'in house' from MeLi.LiBr and HN^iPr_2, the presence of LiBr leads to trifluoroacetate/bromide metathesis and contamination with $[M(\equiv CN^iPr_2)Br(CO)_3(PPh_3)]$. We have therefore devised a synthetic procedure which circumvents these problems.

Fischer has reported the reaction of $[W\{=C(OLi)Ph\}(CO)_5]$ with Br_2PPh_3 to give $[W(\equiv CPh)Br(CO)_4]$ in modest (31%) yield [3]. In applying this idea to the synthesis of aminomethylidyne complexes we find that so long as there is a suitable donor ligand present, aminomethylidyne complexes can be obtained in variable yields depending on the choice of ligand. Thus treatment of $[W(CO)_6]$ with LiN^iPr_2 (25°C), Br_2PPh_3 (−78°C) and PPh_3 (−78 to 25°C) leads to the complex $[W(\equiv CN^iPr_2)Br(CO)_3(PPh_3)]$ [4*] in low yield (30–35%) (Scheme 1 [5*]). It is in practice more convenient not to use preformed Br_2PPh_3, but instead a simple 1:2 mixture of Br_2 and PPh_3 (prepared separately, immediately prior to use), thereby avoiding the isolation of hydrolytically-sensitive reagents. A similar procedure employing Cl_2PPh_3 in place of the dibromide gives $[W(\equiv CN^iPr_2)Cl(CO)_3(PPh_3)]$ [4*]. Both of these complexes serve as convenient air and thermally stable precursors for ligand exchange reactions with, *e.g.*, NaC_5H_5, $K[HB(pz)_3]$ and 1,2-bis(diphenylphosphino)ethane.

Returning to Fischer's synthesis of $[W(\equiv CPh)Br(CO)_4]$ we find that the complex $[W(\equiv CPh)Br(CO)_2(PPh_3)_2]$ may be prepared in 78% yield by employing the Br_2/PPh_3 (1:3.5) reagent. This procedure offers many advantages over established methods, not the least being the use of inexpensive reagents that are of low toxicity and easily manipulated by unsophisticated techniques. We have also extended this approach to the synthesis of the complexes $[W(\equiv C\text{-naphthyl})Cl(CO)_2(tmeda)]$ (57%), $[W(\equiv C\text{-thienyl})Cl(CO)_2$-



Scheme 1.

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* Reference number with asterisk indicates a note in the list of references.

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(tmeda)] (65%), [W(≡C-naphthyl)Cl(CO)$_3$(PPh$_3$)] (67%), [W(≡C-thienyl)Cl(CO)$_3$(PPh$_3$)] (78%) and [W(≡CN^{i}Pr$_2$)Cl(CO)$_2$(2,2′-bipyridyl)] (76%), all of which proceed in good yield (based on 2 g [W(CO)$_6$]). We are currently investigating the extension of this synthetic procedure to other functionalised alkylidyne complexes.

Acknowledgement

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References and notes

1 S. Anderson and A.F. Hill, *J. Organomet. Chem., 394* (1990) C24.
2 For a discussion of the Fischer synthesis see the following reviews: H.P. Kim and R.J. Angelici, *Adv. Organomet. Chem., 27* (1987) 51; A. Mayr and H. Hoffmeister, *Adv. Organomet. Chem., 32* (1992) 227; E.O. Fischer, *Adv. Organomet. Chem., 14* (1973) 1.
3 H. Fischer and E.O. Fischer, *J. Organomet. Chem., 69* (1974) C1.
4 Data for the complexes: (i) [W(≡CN^{i}Pr$_2$)Br(CO)$_3$(PPh$_3$)]: IR (CH_2Cl_2) 2048, 1970, 1931 (CO) 1543 (CN) cm^{-1}.NMR ($CDCl_3$, 25°C, phenyl resonances omitted) ^{1}H; 1.11, [d, 12 H, NCHC*Me*$_2$, *J*(HH) = 6.8 Hz], 2.95 [h, 2 H, NC*H*Me$_2$, *J*(HH) 6.8 Hz]. ^{13}C: 238.2 [d, W≡C, *J*(PC) = 9.0 Hz], 204.7 [d, WCO (*trans* to PPh$_3$) *J*(PC) = 41.0 Hz], 200.6 [d, WCO (*cis* to PPh$_3$), *J*(PC) = 9.0 Hz], 49.1 [N*C*HMe$_2$], 22.0 [NCH*Me*$_2$]; ^{31}P: 17.15 [s, *J*(WP) = 247.4 Hz]. (ii) [W(≡CN^{i}Pr$_2$)Cl(CO)$_3$(PPh$_3$)]: IR (CH_2Cl_2)*ν* 2047, 1969, 1928 (CO) 1541 (CN) cm^{-1}. NMR ($CDCl_3$, 25°C, phenyl resonances omitted) ^{1}H: 1.09 [d, 12 H, NCHC*Me*$_2$, *J*(HH) = 6.8 Hz], 2.87 [h, 2 H, NC*H*Me$_2$, *J*(HH) 6.8 Hz]. ^{13}C: 238.8 [d, W≡C, *J*(PC) = 8.9 Hz], 206.1 [d, WCO (*trans* to PPh$_3$) *J*(PC) = 41.1 Hz], 201.5 [d, WCO (*cis* to PPh$_3$), *J*(PC) = 8.9 Hz], 49.2 [N*C*HMe$_2$], 22.1 [NCH*Me*$_2$]; ^{31}P: 20.0 [s, *J*(WP) = 247.6 Hz]. The formulations were also supported by comparison of data with those for the crystallographically characterised iodo derivative [6].
5 One referee has suggested the possibility of a five-membered intermediate/transition state. We are as yet unable to discount this possibility, although it is not supported by the product stereochemistry (halide *trans* to alkylidyne) and would require prior dissociation of a carbonyl ligand from the phosphorane carbene.
6 A.M.Z. Slawin and D.J. Williams, personal communication.