A Study of the Protonation and Alkylation of *t*-Butyl Isocyanide in *trans*-[M(CNBu-*t*)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (M = Mo or W): Formation of Carbyne-Type Complexes and their *trans*- to *cis*-Isomerization

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Summary

Treatment of complexes *trans*-[M(CNBu-*t*)$_2$(dppe)$_2$][*(1)* M = Mo or W, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$] with protic acid gives a mixture of the aminocarbyne complexes *trans*- plus *cis*-[M(CNHBu-*t*)(CNBu-*t*)(dppe)$_2$]$^+$ *(2)* and the hydridocompounds [MH(CNBu-*t*)$_2$(dppe)$_2$]$^+$ *(3)*, whereas reaction with an alkylating agent (R$^+$) appears to give the dialkylaminocarbyne compounds [M(CNRBu-*t*)(CNBu-*t*)(dppe)$_2$]$^+$ *(4)* also as a mixture of the *trans* and *cis* isomers.

Introduction

Methyl isocyanide, when activated by the electron-rich centres {M(dppe)$_2$} (M = Mo or W), in the complexes *trans*-[M(CNMe)$_2$(dppe)$_2$], is susceptible to attack by an electrophile, particularly the proton (H$^+$) or an alkylating agent (R$^+$). This attack occurs at the nitrogen atom to give carbyne-type complexes, *trans*-[M(CNHMe)(CNMe)(dppe)$_2$]$^+$ or *cis*- and *trans*-[M(CNRMe)(CNMe)(dppe)$_2$]$^+$, respectively[1–4].

However, *t*-butyl isocyanide presents stereochemical and electronic features different from those of methyl isocyanide and it is known[5] to exhibit an anomalous behaviour in some cases. Particularly for *trans*-[M(CNR)$_2$(dppe)$_2$], although an inverse linear relationship between the half-wave oxidation potential ($E^{ox}_{1/2}$) and the energy of the metal → ligand charge transfer band ($1/\lambda_1$) is observed for the aryl isocyanide complexes, which may be rationalised in terms of a simplified π-MO scheme, the inverse trend occurs on passing from CNMe to CNBu-*t* ($E^{ox}_{1/2}$ decreases, as expected, but the same occurs, surprisingly, for $1/\lambda_1$)[6].

Therefore, we undertook a study of the chemical reactivity of the CNBu-*t* complexes *trans*-[M(CNBu-*t*)$_2$(dppe)$_2$] towards electrophiles which would allow a comparison between these compounds and the analogous methyl isocyanide complexes and, hence, to see if large steric bulk of the *t*-Bu group caused any anomalous behaviour.

Results and Discussion

a) Reactions with acids

The complexes *trans*-[M(CNBu-*t*)$_2$(dppe)$_2$] [*(1)* M = Mo or W] react with protic acid (HA) to yield a mixture of the compounds [M(CNHBu-*t*)(CNBu-*t*)(dppe)$_2$]A *(2)* and [MH(CNBu-*t*)$_2$(dppe)$_2$]A *(3)* (Reaction 1).

$$\begin{array}{l} \textit{trans}\text{-[M(CNBu-}t\text{)}_2\text{(dppe)}_2\text{]} + \text{HA} \\ \quad\quad (1) \quad\quad \downarrow \\ \text{[M(CNHBu-}t\text{)(CNBu-}t\text{)(dppe)}_2\text{]A} + \\ \quad\quad\quad (2) \\ \quad\quad \text{[MH(CNBu-}t\text{)}_2\text{(dppe)}_2\text{]A} \\ \quad\quad\quad (3) \end{array} \quad (1)$$

(M = Mo, A = BF_4; M = W, A = BF_4, HSO_4 or FSO_3)

Complexes *(2)* are formed by direct proton attack at the N atom of an isocyanide ligand, activated by the electron-rich metal(0) centre, whereas the formation of the hydrido compounds *(3)* may be explained either by direct protonation of the metal centre (which would compete for the proton with the isocyanide ligand) or, as was observed[1] to occur for methyl isocyanide, by proton migration from the ligating carbyne in *(2)* to the metal.

In the i.r. spectra of complexes [*(2) trans*-isomer], the ν(C≡N) values of the unreacted isonitrile ligand are in the 2140–2120 cm^{-1} range[2] (Table 1) whereas, in the hydrido compounds *(3)*, ν(C≡N) occurs in the 2035–2000 cm^{-1} range[3]. These ν(C≡N) values are comparable to those observed[2, 3] for the analogous CNMe complexes, *e.g.*, *trans*-[Mo(CNHMe)(CNMe)(dppe)$_2$][BF_4] and [MoH(CNMe)$_2$-(dppe)$_2$][BF_4] which exhibit ν(C≡N) at 2163 and 2036 cm^{-1}, respectively.

Complexes *(2)* may occur as mixtures of *trans* with *cis*-isomers (see discussion of the ^{1}H n.m.r. data), and, in the latter, the value of ν(C≡N) (2060 or 2020 cm^{-1} for M = Mo or W, A = BF_4, respectively) is intermediate between those observed for the corresponding *trans*-isomer and the hydride complex. This trend reflects an enhancement of the isocyanide π-acceptance in the *cis*- relative to the *trans*-isomer, due to the weaker competition of a *trans*-phosphine compared to that of a *trans*-carbyne for π-electron density from the metal. The lowest ν(C≡N) value is observed for the hydrido complex, in agreement with the absence of any competing strong π-acceptor carbyne ligand.

Although in the methyl analogues of *(2)*, the carbyne ligand, CNHMe, exhibits ν(C=N) at 1533–1515 cm^{-1} [2], the corresponding band was not observed for the ligating CNHBu-*t* moiety in *(2)* where this band could be buried under others, in the 1490–1400 cm^{-1} range, due to Nujol or to the phosphine phenyl rings, since it would be expected to occur below *ca.* 1480 cm^{-1} by analogy with the related rhenium complexes *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ which have ν(CN) at 1575 cm^{-1} (R = Me) and 1530 cm^{-1} (R = *t*-Bu)[7], *i.e., ca.* 50 cm^{-1} lower for the *t*-butylamino group. These observations suggest, for

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Table 1. Physical data for complexes [M(CNRBu-*t*)(CNBu-*t*)(dppe)$_2$]A (*2* or *4*) and [MH(CNBu-*t*)$_2$(dppe)$_2$]A (*3*).

Complex	Colour	Λ_M[a]	I.r.[b]		Found (Calcd.) %[c]		
			ν(C≡N)	ν(NH)	C	H	N
(2) M = Mo, R = H, A = BF_4	yellowish-green		2140m *(trans)* 2060ms *(cis)*	3260br	64.5(64.9)	5.6(5.8)	2.1(2.4)
(2) M = W, R = H, A = BF_4, HSO_4, FSO_3, BPh_4[d]	green[d]	68–92[d]	2120–2135s[d] *(trans)* 2020–2080s *(cis)*	3260–3270br[d]	[d]		
(3) M = Mo, A = BF_4[e]	[e]	[e]	2035s		[e]		
(3) M = W, A = BF_4, BPh_4[f]			2000–2009s[f]				
(4) M = Mo, R = Me, A = FSO_3	yellow	96 *(trans)*	2143s *(trans)*		64.2(64.5)	5.8(5.9)	2.4(2.4) *(trans)*
		37 *(cis)*[g]	2060s, 2030s[h] } *(cis)*		64.1(64.5)	5.6(5.9)	2.2(2.4) *(cis)*
(4) M = W, R = Me, A = FSO_3	yellow	77 *(trans)*	2135s *(trans)*		60.0(60.0)	5.7(5.5)	2.0(2.2) *(trans)*
		75 *(cis)*	2050s, 2020s[h] } *(cis)*		59.7(60.0)	5.4(5.5)	2.0(2.2) *(cis)*
(4) M = W, R = Et, A = BF_4[i]	yellow	90 *(cis)*	2050s, 2020s[h] } *(cis)*		57.7(57.9)	5.2(5.5)	2.3(2.1)

[a] In *ca.* 10^{-3} M $MeNO_2$ solution ($\Omega^{-1}cm^2mol^{-1}$). [b] In Nujol mull (values in cm^{-1}). [c] Required values in parentheses. [d] Already quoted (ref. 2). [e] Mixed with *trans*- and *cis-(2)* (M = Mo, R = H, A = BF_4) (see these complexes). [f] Already quoted (ref. 3); ν(W–H) = 1910w,br (for A = BF_4). [g] In *ca.* 10^{-3} M $(ClCH_2)_2$ solution. [h] Variable relative intensity (two *cis*-isomers). [i] With CH_2Cl_2 of crystallization.

this ligand, a higher contribution of the carbyne (A) over the carbene (B) resonance form, in the following V. B. representation:

$$\{\overset{+}{M}\equiv C\text{–}NHBu\text{-}t\} \leftrightarrow \{\overset{+}{M}=C=NHBu\text{-}t\}$$
(A) (B)

The greater electron releasing ability of CNBu-*t* compared to CNMe, which would favour electron acceptance of the carbyne ligand, CNHBu-*t*, from the metal centre, may conceivably play a role in this relative behaviour (between the CNHBu-*t* and the CNHMe ligands).

Variable temperature ^{1}H n.m.r. studies of [*(2, 3);* M = Mo; A = BF_4] were performed in CD_2Cl_2 and the data obtained (Table 2) were interpreted by considering the occurrence of the following equilibra (a) and (b):

trans-[Mo(CNHBu-*t*)(CNBu-*t*)(dppe)$_2$]BF_4
[trans-(2)]

(a) ⇃↾ ⇂↿ (b)

cis-[Mo(CNHBu-*t*)(CNBu-*t*)-(dppe)$_2$]BF_4 *[cis-(2)]* [MoH(CNBu-*t*)$_2$(dppe)$_2$]BF_4 *(3)*

The presence of the *cis* isomer of carbyne complex *(2)* was recognized by the detection of two phenyl triplets (J = 9.0 Hz, δ 6.55 and 6.03 ppm, at 25 °C), upfield from the bulk of the complex phenyl resonance, which may be assigned to the four *ortho*-phenyl protons of two phenyl rings (one in each dppe ligand) in the *cis*-configuration by analogy with other *cis*-hexacoordinate bis(dppe) complexes such as *cis*-[M(CO)$_2$(dppe)$_2$] (M = Cr, Mo or W)[7], *cis*-[IrS_2(dppe)$_2$]Cl[8] and *cis*-[M(CNRMe)(CNMe)(dppe)$_2$]A (M = Mo or W, R = Me, A = FSO_3; M = W, R = Me, A = $MeSO_4$)[4].

From analysis of the x-ray structural data on the above iridium complex, the upfield shift of the four *ortho*-phenyl proton resonance is believed[8] to be due to their interaction with the two *cis*-non-phosphorus ligands.

Each triplet resonance in complexes *(2)* is believed to be the result of the overlap of two doublets (one by coupling with the phosphorus nucleus and the other by coupling with the *meta*-phenyl protons) and the observed coupling constant (J = 9.0 Hz) is comparable to those quoted for the above mentioned *cis*-dppe complexes.

The occurrence of the equilibrium between the *cis*- and the *trans*-isomers was evidenced by variable temperature ^{1}H n.m.r. data.

Thus, cooling the n.m.r. solution to −40 °C results in an increase of the intensity (to about double of that observed at *ca.* 25 °C) of the *ortho*-phenyl triplets and of two singlet *t*-Bu proton resonances (δ 1.16 and 0.64 ppm, at 25 °C) which are, thus, assigned to the *cis*-isomer. This occurs mainly at the expense of two other *t*-Bu singlet resonances (with equal integration at δ 0.48 and 0.41 ppm, at 25 °C) which are assigned to the *trans*-isomer. A singlet observed at δ 0.05 ppm (25 °C) also decreases in intensity upon cooling, but only slightly and it is assigned to the two equivalent *t*-Bu groups of the hydride complex *(3)* which displays a broad hydride resonance at *ca.* −6.0 ppm.

By taking also in consideration the relative intensities, among the various complexes, of the *t*-Bu proton resonances, and the integration of the *ortho*-phenyl triplets of the *cis*-isomer (given in Table 2), the following conclusions may be drawn:

At 25 °C, the relative proportions of the *cis*- and the *trans*-carbyne complexes [*(2)* M = Mo, A = BF_4] and the corresponding hydrido compound *(3)* are *ca.* 0.22:0.28:0.50, respectively; however, upon cooling to −40 °C, the amount of the *cis*-isomer of [*(2)* M = Mo, A = BF_4] increases mostly at the expense of the corresponding *trans* complex *(2)* and, to a smaller extent, of the hydride compound *(3)*, their relative propor-

Table 2. ^{1}H n.m.r. data[a] for complexes [M(CNHBu-*t*)(CNBu-*t*)(dppe)$_2$]A *(2)* and [MH(CNBu-*t*)$_2$(dppe)$_2$]A *(3)*.

Complex	Temp. (°C)	δ	Integration		Assignment
(2 + 3) (M = Mo, A = BF_4)	25	7.9–6.9m			dppe aromatic
		6.55t[b]	*ca.* 0.5(0.44)	40(40)	*cis-(2)*
		6.03t[b]	*ca.* 0.5(0.44)		
		ca. 4.0br	*ca.* 0.5(0.5)		CN*H*Bu-*t*
		3.6–2.6mbr	8(8)		dppe methylene
		1.16s	2(2)		CNHBu-*t* *cis-(2)*
		0.64s	2(2)		CNBu-*t* *cis-(2)*
		0.48s	2.5(2.5)		CNHBu-*t* *trans-(2)*
		0.41s	2.5(2.5)		CNBu-*t* *trans-(2)*
		0.05s	9(9)		CNBu-*t* *(3)*
		ca. –6.0br	(0.5)		hydride *(3)*
	–40	8.1–6.5m			dppe aromatic
		6.54t[b]	*ca.* 1(0.9)	40(40)	*cis-(2)*
		5.82t[b]	*ca.* 1(0.9)		
		ca. 3.9br	*ca.* 0.5(0.6)		CNHBu-*t*
		3.4–2.4mbr	8(8)		dppe methylene
		1.08s	4(4)		CNHBu-*t* *cis'-(2)*
		0.52s	4(4)		CNBu-*t* *cis'-(2)*
		0.40s	1.3(1.3)		CNHBu-*t* *t-trans-(2)*
		0.34s	1.3(1.3)		CNBu-*t* *t-trans-(2)*
		0.01s	7.5(7.4)		CNBu-*t* *(3)*
		ca. –6.1br	(0.4)		hydride *(3)*
(2) + *(3)* (M = W, A = BPh_4)	–40	8.1–6.4m			dppe aromatic + BPh_4
		6.04t[b]	*ca.* 1.5(1.6)	60(60)	
		4.5–2.0m	8(8)		dppe methylene
		1.16s	7		CNHBu-*t* *cis-(2)*
		0.62s	7		CNBu-*t* *cis-(2)*
		0.50s	4		CNBu-*t* *(3)*
		ca. –3mbr[c]	*ca.* 0.2(0.2)		hydrido *(3)*

[a] In CD_2Cl_2, δ values relative to internal TMS; [b] J = 9.0 ± 0.5 Hz (*cis*-isomer); [c] At –70 °C, *ca.* –5mbr.

tions becoming *ca.* 0.44:0.14:0.42. Hence, shifts of equilibria (a) and (b) (see above) towards the *trans* to *cis* conversion of the carbyne complex and, to a smaller extent, towards the conversion of the corresponding hydride *(3)* into the *trans* carbyne complex, result from lowering the temperature.

In the solid state, the *tungsten* carbyne complexes *(2)* are also mixtures of both the *trans*- and the *cis*-isomer, but the latter is the only detected isomer in solution [at –40 °C, for *(2)* A = BPh_4]. The presence of the *cis*-isomer is evidenced by the phenyl triplet (δ 6.04 ppm, J = 9.0 Hz, in CD_2Cl_2) which is observed up-field from the other phenyl proton resonances (Table 2).

On account of decomposition and/or low solubility in normal solvents, no reliable or informative ^{31}P n.m.r. spectra were recorded. They consisted mainly of complex patterns, *e.g.*, in the 88.9–121.9 ppm range, upfield from trimethylphosphite, for the mixture of *(2)* with *(3)* (M = W, A = BPh_4).

The formation of the *cis*-isomers of complexes *(2)* may be interpreted on the basis of the strong π-electron-acceptor character of the carbyne ligand. In the *trans*-isomers, the *trans*-ligand, an isocyanide, competes strongly with the carbyne for the available metal *d* electrons. In the *cis*-isomer, however, a much weaker electronic competition of this type occurs on account of the weaker π-electron-acceptor ability of tertiary phosphine compared to isocyanide. Since the formation of the *cis*-isomer was not observed in the methyl isocyanide complexes analogous to *(2)*, in spite of the smaller dimension of the methyl compared to the *t*-butyl group, it appears that in the *trans* to *cis* rearrangement, electronic effects dominate over the potentially unfavourable steric interactions of the bulky *t*-Bu groups. The higher electronic σ-release of CNBu-*t*, relative to CNMe, opposes carbyne stability in *trans* structure in a stronger way for the *t*-butylaminocarbyne complexes.

Moreover, a similar rearrangement appears to occur in the related dialkylaminocarbyne complexes *(vide infra)* formed by alkylation of compounds *(1)*.

b) Reactions with an alkylating agent

Treatment of the isocyanide complexes *(1)* with $MeFSO_3$ in benzene causes the alkylation of one of the *t*-butyl isocyanide ligands to give the dialkylaminocarbyne complexes [M(CNRBu-*t*)(CNBu-*t*)(dppe)$_2$]A [*(4)* R = Me, A = FSO_3] as yellow precipitates which are a mixture of the *trans*- with the *cis*-isomer in variable relative amounts.

If the alkylation reaction is carried out in CH_2Cl_2, the species isolated from solution are a mixture of both isomers for $MeFSO_3$ (M = Mo or W) or the pure *cis*-isomers for Et_3OBF_4, M = W (Equation 2).

$$\textit{trans}\text{-[M(CNBu-}t\text{)}_2\text{(dppe)}_2\text{]} + \text{RA} \rightarrow \text{[M(CNRBu-}t\text{)(CNBu-}t\text{)(dppe)}_2\text{]A } \textit{(4)} \quad (2)$$

(M = Mo or W; RA = $MeFSO_3$; M = W, RA = Et_3OBF_4)

Complexes *(4)* are, as expected, ionic in solution (1:1 electrolytes) (Table 1) and also in the solid state since no departure from C_{3v} symmetry of the FSO_3^- counterion was detected in the infrared spectra which exhibit bands associated with

ionic fluorosulphate[9] at *ca.* 1285 vs [$\nu_{asym}(SO_3)(E)$], 1065 ms [$\nu_{sym}(SO_3)(A_1)$] and 585 ms [$\delta_{asym}(SO_3)(E)$]. The expected [$\nu(SF)$] absorption at *ca.* 760 cm^{-1} was buried under the dppe bands.

In the i.r. spectra (Table 1), $\nu(C{\equiv}N)$ of the unreacted isocyanides (*trans*-isomers, 2143–2135 cm^{-1}) are similar to those observed in the corresponding carbyne complexes *(2)*. In the *cis*-isomers, the i.r. C≡N stretching mode occurs at a lower value (in the 2060–2020 cm^{-1} range), in agreement with the weaker π-electron competition of the *trans*-phosphine compared to that of *trans*-carbyne in the *trans*-isomers, as observed for the corresponding complexes *(2)*.

In the *cis*-complexes *(4)*, two i.r. absorptions are observed for the unreacted isocyanide ligand, in slightly variable relative intensity within distinct preparations and/or recrystallizations, which may be interpreted by considering them as mixtures of two isomers in variable proportions; in pyridine solution the isomer with lower $\nu(C{\equiv}N)$ predominates and the absorption of the other isomer is observed only as a very weak shoulder on the band of the former.

Unfortunately, it was not possible to collect n.m.r. data for complexes *(4)* since they were not sufficiently soluble in convenient solvents.

Although the *trans*-isomers of complexes *(4)* are conceivably the initial products of the alkylation of the *trans*-bisisocyanide complexes *(1)*, the formation of the *cis*-isomers may be rationalized in the same way as suggested for the corresponding compounds *(2)* obtained from protonation reactions, namely the lesser competition with the carbyne ligand for π-electron density by the *trans* co-ligand in the *cis*-isomers.

Final comments

As observed for methyl isocyanide, the strong π-electron donor ability of the electron-rich {$M(dppe)_2$} (M = Mo or W) centre activates a *t*-butyl isocyanide ligand, in complexes of the type *trans*-[$M(CNR)_2(dppe)_2$], towards ready attack by an electrophile to give carbyne-type complexes.

In agreement with the expected lower π-acceptor character of CNBu-*t* compared to CNMe, only one of the *t*-butyl isocyanide ligands undergoes electrophilic attack, whereas both methyl isocyanide ligands can be protonated by acid. Moreover, an the basis of infrared data, the *t*-butylaminocarbyne ligand appears to present a higher carbyne character than the methylaminocarbyne ligand, which is also in accordance with the expected lower competion, for the metal π-electron release, of CNBu-*t* in the former case compared to the CNMe co-ligand in the latter; moreover, the stronger electron σ-release of the *t*-Bu group, relative to Me, promotes metal π donation to the carbyne ligand.

A *trans* to *cis* isomerization of all types of *t*-butylaminocarbyne complexes occurs, whereas for the methylaminocarbyne compounds such an isomerization was detected only for the products of alkylation. These observations suggest that, for this isomerization, electronic effects (resulting in the competition of the isocyanide and the carbyne ligand towards the metal π release) are prominent over stereochemical ones and that the greater σ-release of CNBu-*t*, compared to CNMe, opposing that of the carbyne is an additional destabilizing factor.

Experimental

All the reactions were carried out using standard inert gas flow and vacuum techniques. Solvents were purified by standard techniques and the complexes *trans*-[$M(CNBu\text{-}t)_2(dppe)_2$][*(1)* M = Mo or W][10] were prepared by published methods. Fluoroboric acid (Et_2O complex) and methyl fluorosulphate were used as purchased and [Et_3O][BF_4] was prepared by a literature procedure[11].

I.r. measurements were carried out on a Perkin-Elmer 683 or 577 spectrometer and ^1H n.m.r. spectra were recorded on a Bruker CXP 300 or a Jeol PS100 spectrometer equipped with a 546 J Digital Signal Averager. Conductivities were measured using a Portland Electronics P310 conductivity bridge.

Reaction of trans-[M(CNBu-t)$_2$(dppe)$_2$] [(1) M = Mo or W] with acid

Since the methods used are general, only an example using HBF_4 (as [Et_2OH][BF_4]) (for M = Mo) is given.

Fluoroboric acid (0.275 cm^3 of a Et_2O solution obtained by 1:21 dilution of [Et_2OH][BF_4]; 0.094 mmol of acid) was added dropwise to a stirred solution of complex *(1)* (M = Mo) (0.110 g, 0.104 mmol) in PhH (11 cm^3). The resulting yellowish green precipitate of complexes *(2)* and *(3)* (M = Mo, A = BF_4) was filtered-off, washed with PhH and dried *in vacuo* (*ca.* 0.050 g, 42%).

The replacement of the anion in any complex *(2)* by BPh_4^- can be achieved by reaction, in thf, with an excess of $NaBPh_4$ followed by evaporation of the solution to dryness and extraction by CH_2Cl_2; filtration of the solution and addition of Et_2O led to the precipitation of the final product [*(2)* A = BPh_4].

Reaction of trans-[M(CNBu-t)$_2$(dppe)$_2$][(1) M = Mo or W] with methyl fluorosulphate

$MeFSO_3$ (0.151 cm^3, 1.91 mmol) was added to a solution of complex *(1)* M = Mo (0.253 g, 0.239 mmol) in PhH (25 cm^3) and the reaction solution was stirred overnight. A greenish yellow precipitate was formed, a mixture of *trans*- with *cis*-[Mo(CNMeBu-*t*)(CNBu-*t*)$(dppe)_2$]FSO_3 [*(4)* M = Mo, R = Me, A = FSO_3] (0.112 g, 40% yield), which was filtered-off, washed with PhH and dried *in vacuo*. Concentration of the mother liquor and cooling at *ca.* −10 °C gave the pure yellow crystalline *cis*-isomer (0.140 g, 50%). The tungsten analogous complexes were prepared by the same procedure, *mutatis mutandis*.

Reaction of trans-[W(CNBu-t)$_2$(dppe)$_2$] [(1) M = W] with [Et$_3$O][BF$_4$]

$Et_3O^+BF_4^-$ (0.170 g, 0.895 mmol) was added to a CH_2Cl_2 solution (10 cm^3) of complex *(1)* M = W (0.340 g, 0.296 mmol). After stirring overnight, concentration to *ca.* 6 cm^3 followed by addition of MeOH (25 cm^3) gave *cis*-[W(CNEt-Bu-*t*)(CNBu-*t*)$(dppe)_2$]BF_4 [*(4)* M = W, R = Et, A = BF_4] as yellow crystals which were filtered-off, washed with MeOH and dried *in vacuo*. Further crops of yellow crystals of the same complex were obtained by concentration of the mother liquor (total 0.359 g, 90%).

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