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THE SUBSTITUTION REACTIONS OF *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) AND *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ WITH ISONITRILES: AN NMR STUDY

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Summary

Isonitriles, RNC (R = Me, t-Bu or C_6H_4Me-4) displace dinitrogen quantitatively from *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) and *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ in benzene under tungsten light irradiation. For *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ the stepwise formation of the complexes *trans*-$[M(CNR)_2(PMe_2Ph)_4]$, *cis*-$[M(CNR)_2(PMe_2Ph)_4]$, *mer*-$[M(CNR)_3(PMe_2Ph)_3]$ and *cis*-$[M(CNR)_4(PMe_2Ph)_2]$ has been established using NMR spectroscopy of the reaction solutions. For *trans*-$[Mo(N_2)_2(PMePh_2)_4]$, the only products characterised by NMR spectroscopy were *mer*-$[Mo(CNR)_3(PMePh_2)_3]$ and *trans*-$[Mo(CNR)_4(PMePh_2)_2]$.

We have shown that quantitative displacement of the dinitrogen ligands of *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W) by isonitriles gives the complexes *trans*-$[M(CNR)_2(Ph_2PCH_2CH_2PPh_2)_2]$ [1] in which the ligating isonitrile shows reactivity towards electrophilic attack [2,3]. In order to extend the range of our studies, we have investigated similar displacement reactions using the dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[Mo(N_2)_2(PMePh_2)_4]$. We find, as expected, that isonitriles RNC (R = Me, t-Bu or C_6H_4-Me-4) quantitatively displace the dinitrogen from these complexes, but the reaction is more complicated than that observed with complexes of the chelating diphosphine ligands because substitution of the monodentate phosphines also occurs.

The products of these reactions were very difficult to isolate, being oils, probably because of unavoidable contamination with traces of displaced ter-

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tiary phosphine. We were, however, able to monitor the course of these reactions by ^1H and ^{31}P NMR spectroscopy by carrying out the reactions in $C_6{}^2H_6$ solution under irradiation with tungsten light in NMR tubes.

Results and discussion

A) NMR spectroscopic data and reaction schemes

The course of the reactions is shown in Scheme 1. The components of the scheme were established by use of the NMR data shown in Tables 1 and 2 and the interpretation of these data is discussed below.

The reactions were carried out by adding, under dinitrogen, a measured quantity of isonitrile to a solution of the appropriate dinitrogen complex in $C_6{}^2H_6$ in a NMR tube, followed by irradiation with a 100 W tungsten-filament bulb. In initial experiments 1 mole of isonitrile per metal atom was added in an attempt to obtain the singly-substituted complex. Such a complex was never observed, however, but only compounds in which all the dinitrogen had been displaced. More generally 2 moles of isonitrile per metal atom were added and the reaction monitored by NMR spectroscopy until no free isonitrile remained in solution. Further measured quantities of isonitrile were then added and the reaction monitored until replacement of both dinitrogen molecules and up to two phosphine ligands had occurred. The extent of substitution of phosphine depended upon the group R of the isonitrile and upon the phosphine. Thus CNC_6H_4Me-4 can displace two phosphine ligands from the dinitrogen complexes. MeNC can displace one phosphine from all the dinitrogen complexes, and up to two $PMePh_2$ ligands, but t-BuNC is only able to displace one phosphine. The inability of t-BuNC to induce further substitution is probably steric in origin. CNC_6H_4Me-4 is the best π-acceptor of these isonitriles and also achieves the most substitution. This suggests that the π-acceptor ability of the isonitrile is important in labilising phosphine at these metal sites.

The presence of displaced tertiary phosphine in solution has precluded the

SCHEME 1. SUBSTITUTION REACTIONS OF *cis*-$[M(N_2)_2P_4]$ (M = Mo or W) AND *trans*-$[Mo(N_2)_2P'_4]$ WITH ISONITRILES

cis-$[M(N_2)_2P_4]$ + 2 CNR $\xrightarrow{-2N_2}$ *trans*-$[M(CNR)_2P_4]$ [M = Mo; R = Me, C_6H_4Me-4, t-Bu] $\rightarrow$ *cis*-$[M(CNR)_2P_4]$ [M = Mo, W, R = Me, C_6H_4-4; M = Mo, R = t-Bu [a]]

CNR $\longrightarrow$ *mer*-$[M(CNR)_3P_3]$ + P $\xrightarrow{CNR}$ *cis*-$[M(CNR)_4P_2]$ + 2 P

mer-$[M(CNR)_3P_3]$: [M = Mo, W, R = Me, C_6H_4Me-4; M = W, R = t-Bu [b]]

cis-$[M(CNR)_4P_2]$: [M = W, R = C_6H_4Me-4]

trans-$[Mo(N_2)_2P'_4]$ + 3 CNR $\xrightarrow{-2N_2}$ *mer*-$[Mo(CNR)_3P'_3]$ + P' [R = Me, C_6H_4Me-4, t-Bu]

mer-$[Mo(CNR)_3P'_3]$ $\xrightarrow{CNR}$ *trans*-$[Mo(CNR)_4P'_2]$ + 2 P' [R = Me, C_6H_4Me-4]

[P = PMe_2Ph, P' = $PMePh_2$]

[a] Always in a smaller amount than the *trans*-isomer.
[b] *Facial* isomer also formed.

isolation of analytically pure complexes, red oils are always obtained on solvent removal. A similar problem was also encountered when *trans*-[$Mo(N_2)_2(PMePh_2)_4$] and *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] were treated with carbon monoxide. Although *mer*-[$Mo(CO)_3(PMePh_2)_3$] (obtained from reaction with carbon monoxide at —78°C), *cis*-[$Mo(CO)_4(PMePh_2)_2$] (from reaction at 20°C) and *fac*-[$Mo(CO)_3(PMe_2Ph)_3$] (from reaction at 20°C) were observed in solution, their attempted isolation gave only red oils [4].

TABLE 1

^{31}P NMR (PROTON NOISE DECOUPLED) DATA FOR [$M(CNR)_xL_{6-x}$](L = PMe_2Ph, $PMePh_2$)

Complex	δ [a]	Assignment	—Δ [b]	$\|^2J(PP')\|$ [c]	$^1J(W-P)$ [d]
cis-[$W(CNMe)_2(PMe_2Ph)_4$]	159.5t	[e]	27.9	14.7	275.9
	164.1t	[f]	23.2		216.0
mer-[$W(CNMe)_3(PMe_2Ph)_3$]	153.3d	[e]	34.0	14.6	280.8
	162.5t	[f]	24.9		218
cis-[$W(p\text{-TolNC})_2(PMe_2Ph)_4$]	159.1t	[e]	28.3	16.5	268.6
	167.1t	[f]	20.2		190.4
mer-[$W(p\text{-TolNC})_3(PMe_2Ph)_3$]	154.7d	[e]	32.7	16.8	274.5
	165.2t	[f]	22.2		198.0
cis-[$W(p\text{-TolNC})_4(PMe_2Ph)_2$]	163.8s	[e]	23.5		197.9
mer-[$W(CNt\text{-Bu})_3(PMe_2Ph)_3$]	162.5d	[e]	24.8	10.4	297.9
	166.3t	[f]	21.0		268.5(?)
fac-[$W(CNt\text{-Bu})_3(PMe_2Ph)_3$]	161.4s	[e]	25.9		293.0
trans-[$Mo(CNMe)_2(PMe_2Ph)_4$]	124.5s	[e]	62.8		
cis-[$Mo(CNMe)_2(PMe_2Ph)_4$]	128.9t	[e]	57.5	20.8	
	140.7t	[f]	46.7		
mer-[$Mo(CNMe)_3(PMe_2Ph)_3$]	124.8d	[e]	62.6	21.2	
	137.2t	[f]	50.2		
trans-[$Mo(p\text{-TolNC})_2(PMe_2Ph)_4$]	126.9s	[e]	60.4		
cis-[$Mo(p\text{-TolNC})_2(PMe_2Ph)_4$]	131.3t	[e]	56.0	22.0	
	146.5t	[f]	40.9		
mer-[$Mo(p\text{-TolNC})_3(PMe_2Ph)_3$]	127.2d	[e]	60.2	22.0	
	142.4t	[f]	45.0		
trans-[$Mo(CNt\text{-Bu})_2(PMe_2Ph)_4$]	128.6s	[e]	58.8		
cis-[$Mo(CNt\text{-Bu})_2(PMe_2Ph)_4$]	132.2t	[e]	55.2	19.5	
	142.2t	[f]	45.1		
mer-[$Mo(CNMe)_3(PMePh_2)_3$]	105.2d	[e]	62.8	19.5	
	117.4t	[f]	50.5		
trans-[$Mo(CNMe)_4(PMePh_2)_2$]	103.2s	[e]	64.8		
mer-[$Mo(p\text{-TolNC})_3(PMePh_2)_3$]	107.8d	[e]	60.2	19.5	
	122.0t	[f]	45.9		
trans-[$Mo(p\text{-TolNC})_4(PMePh_2$]	105.6s	[e]	62.3		
mer-[$Mo(CNt\text{-Bu})_3(PMePh_2)_3$]	107.2d	[e]	60.7	17.1	
	119.5t	[f]	48.4		

[a] In C_6D_6 at 25°C, ppm upfield from internal TMP. Integration values always agree with the expected ones. [b] $\Delta = \delta - \delta$ (free phosphine) = phosphine downfield co-ordination shift. [c] P and P' refer to lower and higher field resonances respectively. Values in Hz ± 1.2 Hz. [d] First value for $^1J(W-P)$. Second one for $^1J(W-P')$. Values in Hz ± 1.2 Hz. [e] Phosphine *trans* to phosphine. [f] Phosphine *trans* to isonitrile.

^{31}P NMR spectra (Table 1)

This technique proved to be the most useful one, because of the wide range of chemical shifts involved and the sensitivity of the NMR pattern observed to the geometry of the complexes, compared to ^{1}H NMR spectra on the same systems (Table 2).

The diagnostic features of the spectra are:

I. *cis*-$[M(N_2)_2(PMe_2Ph)_4]$

a) For M = Mo, one singlet which replaces the initial resonance pattern of the parent bis(dinitrogen) complex upon addition of CNR in a molar ratio not greater than 2 CNR/metal atom, is assigned to *trans*-$[Mo(CNR)_2(PMe_2Ph)_4]$. A tungsten analogue was not observed.

b) After further time, the initially-observed singlet of *trans*-$[Mo(CNR)_2(PMe_2Ph)_4]$ is replaced by two equally intense triplets, assigned to *cis*-$[Mo(CNR)_2(PMe_2Ph)_4]$. The same pattern was also observed in the reaction of the tungsten analogue rather than a singlet, probably because the *trans—cis* conversion is more rapid in this case.

c) On addition of more isonitrile (up to 3 CNR per M atom) the two triplets are replaced by a doublet and a triplet (intensity ratio 2 : 1), together with a singlet at higher field due to free PMe_2Ph [the relative integrations were 2(doublet) : 1(triplet) : 1 (free PMe_2Ph)]. The doublet-plus-triplet pattern is assigned to *mer*-$[M(CNR)_3(PMe_2Ph)_3]$.

d) On addition of an excess of CNC_6H_4Me-4 (M = W) the *mer*-pattern was replaced by a singlet, due to *cis*-$[W(CNC_6H_4\text{-}4)_4(PMe_2Ph)_2]$ (see below) and the appropriate increase of intensity of the resonance due to free PMe_2Ph, to give a final 1 : 1 integration ratio of free to ligating PMe_2Ph.

e) On addition of an excess of t-BuNC to *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ two singlets replace the resonances of the dinitrogen complex, with a relative integration ratio of 3 : 1. The higher-field resonance has the lower intensity and is due to free PMe_2Ph, the other resonance is assigned to *fac*-$[W(CNt\text{-}Bu)_3(PMe_2Ph)_3]$. Further substitution does not occur.

II. *trans*-$[Mo(N_2)_2(PMePh_2)_4]$

The first detected products of reaction of RNC with this dinitrogen complex are *mer*-$[Mo(CNR)_3(PMePh_2)_3]$, characterised by the two (doublet) : one (triplet) : one (free $PMePh_2$) pattern discussed above for the PMe_2Ph analogue. On addition of more isonitrile (CNC_6H_4Me-4), the doublet-triplet pattern decreases and is replaced by a singlet, with simultaneous growth of the free $PMePh_2$ resonance. The new singlet resonance is assigned to the complex *trans*-$[Mo(CNC_6H_4Me\text{-}4)_4(PMePh_2)_2]$, since the ^{1}H spectrum (see below and Table 2) shows the triplet PCH_3 pattern diagnostic of *trans*-phosphines.

Chemical shifts

The usual downfield shifts [5] (Δ, Table 1) of the ^{31}P resonance of tertiary phosphine upon ligation is observed, being greater for molybdenum than tungsten, as has been observed for *trans*-$[M(CNt\text{-}Bu)_2(dppe)_2]$ [1] and in related complexes [5]. The coordination shift (Δ) is not appreciably dependent upon the chemical shift of the free phosphine, since shifts for $PMePh_2$ and PMe_2Ph are very similar, although the free ligands have different chemical shifts [167.9 and 187.3 ppm relative to $P(OMe)_3$, respectively].

Within the series of complexes reported here, the absolute magnitude of Δ depends upon the complex in the order *trans*-$[M(CNR)_2L_4]$ > *mer*-$[M(CNR)_3L_3]$ > *cis*-$[M(CNR)_2L_4]$ (L = tertiary phosphine). For analogous complexes of this series, Δ varies with R in the order Me > t-Bu, CNC_6H_4Me-4.

Coupling constants

In meridional complexes ^1J(WP) for the *trans*-tertiary phosphine ligands is greater than that for the phosphorus which is *trans* to isonitrile. This can be rationalised in terms of a weaker π-acceptance for the phosphorus *trans* to the more strongly π-accepting isonitrile ligand, thus leading, by a synergic effect, to a weaker W—P σ-interaction. Thus the *s*-overlap integral for the W—P bond upon which the coupling constant depends, is reduced. A similar trend has been observed [6] in isomers of $[W(CO)_4L_2]$ (L = PBu_3 or $PBuPh_2$). These results suggest the order of σ-*trans*-influence in hexa-coordinated complexes of W^0 to be: CNR, CO > tertiary phosphine. This order is the opposite to that observed for square-planar complexes of Pt^{II} and octahedral complexes of Pt^{IV}, where π-effects are probably low [7].

Based upon these observations, the lower field triplet of *cis*-$[W(CNR)_2(PMe_2Ph)_4]$ (R = Me or CNC_6H_4Me-4) is assigned to the *trans*-phosphines, since ^1J(WP) is greater than that of the higher-field triplet. The *cis*-configuration for $[W(CNC_6H_4Me\text{-}4)_4(PMe_2Ph)_2]$, proposed earlier, is based upon its low ^1J(WP) value, indicating that isonitrile is *trans* to phosphorus.

All the ^2J(PP) couplings observed in this study involve *cis*-phosphorus nuclei. Their absolute magnitude is mainly dependent upon the metal, being greater for Mo than for W complexes (Table 1) as is commonly observed for Group VI metal complexes (Cr > Mo > W) [8].

^1H NMR spectra (Table 2)

Although the resonance of free-isonitrile (1 : 1 : 1 triplet, J(NH) 2.3 Hz, R = Me; 2.0 Hz, R = t-Bu) and free tertiary phosphine (doublet, ^2J(PH) 3.4 Hz, PMe_2Ph, and 3.9 Hz, $PMePh_2$) would be clearly observed, the assignment of resonances of the coordinated ligands was complicated by their overlap. Nevertheless, the characteristic P—Me pattern of phosphine ligands could be used to assign *cis* or *trans* geometries in a number of cases (Table 2).

Thus in *trans*-$[Mo(CNR)_2(PMe_2Ph)_4]$ a broad singlet resonance appears for all the equivalent P-CH_3 groups, whereas in *cis*-$[Mo(CNR)_2(PMe_2Ph)_4]$ a triplet is seen for the *trans*-phosphines, together with a higher field filled-in doublet pattern due to the *cis*-phosphines [9]. In meridional complexes the methyl resonances of the phosphine ligands consist of the expected triplet for the *trans*-phosphines and a doublet for a unique phosphine, at higher field. In *trans*-$[M(CNR)_4L_2]$ (L = tertiary phosphine), the PCH_3 resonance is a triplet.

Only a singlet is observed for the $CNC_6H_4CH_3$-4 resonances of *mer*-$[Mo(CNC_6H_4Me\text{-}4)_3(PMe_2Ph)_3]$, perhaps because the chemical shift separation is too small to be measured. Similar behaviour has been observed in *cis*-$[Mo(CNMe)_4(CO)_2]$ whose $CNCH_3$ resonance is a singlet, whereas the CNt-Bu analogue shows the expected two equally intense t-Bu resonances [10].

All the complexes studied show a downfield shift of the PCH_3 resonance and an increase of $|^2J(PH)|$, relative to the values in the free phosphine. Downfield

TABLE 2

^{1}H NMR DATA ON [M(CNR)$_x$L$_{6-x}$] (L = PMe_2Ph and $PMePh_2$)

Complex	δ [a] ±0.02	Integration [b]	Assignment	$\lvert^2J(PH)\rvert$ ±0.5 Hz [c]
cis-[W(CNMe)$_2$(PMe_2Ph)$_4$	7.7—6.7m	20(20)	PMe_2*Ph*	
	2.90s	5(6)	CN*Me*	
	1.67t	12(12)	*trans*-P*Me*$_2$Ph	2 X 2.2
	1.48fd	11(12)	P*Me*$_2$Ph *trans* to CNR	4.2
mer-[W(CNMe)$_3$(PMe_2Ph)$_3$]	7.6—6.9m	15(15)	PMe_2*Ph*	
	3.05s	3(3)	CN*Me trans* to P	
	2.88s	5(6)	*trans*-CN*Me*	
	1.88t	12(12)	*trans*-P*Me*$_2$Ph	2 X 2.8
	1.35d	6(6)	P*Me*$_2$Ph *trans* to CNMe	5.9
cis-[W(*p*-TolNC)$_2$(PMe_2Ph)$_4$]	7.5—6.6m	28(28)	PMe_2*Ph* + $CNC_6H_4CH_3$	
	2.17s	6(6)	CNC_6H_4*C*H_3	
	1.70t	12(12)	*trans*-P*Me*$_2$Ph	2 X 2.8
	1.43fd	12(12)	P*Me*$_2$Ph *trans* to CNR	5.0
trans-[Mo(CNMe)$_2$(PMe_2Ph)$_4$]	8.0—6.8m	20(20)	P*Me*$_2$Ph	
	3.00s	6(6)	CN*Me*	
	1.52s	23(24)	P*Me*$_2$Ph	
cis-[Mo(CNMe)$_2$(PMe_2Ph)$_4$]	7.7—6.6m	20(20)	P*Me*$_2$Ph	
	2.75s	5.5(6)	CN*Me*	
	1.50t	11(12)	*trans*-P*Me*$_2$Ph	2 X 2.3
	1.32fd	12(12)	P*Me*$_2$Ph *trans* to CNR	4.0
mer-[Mo(CNMe)$_3$(PMe_2Ph)$_3$]	7.8—7.0m	15(15)	P*Me*$_2$Ph	
	2.90s	3(3)	CN*Me trans* to P	
	2.78s	5.5(6)	*trans*-CN*Me*	
	1.72t	12(12)	*trans*-P*Me*$_2$Ph	2 X 2.5
	1.17d	7(6)	P*Me*$_2$Ph *trans* to CNR	4.7
trans-[Mo(*p*-TolNC)$_2$(PMe_2Ph)$_4$]	7.8—6.6m	28(28)	PMe_2*Ph* + $CNC_6H_4CH_3$	
	2.16s	6(6)	CNC_6H_4*C*H_3	
	1.61s	22(24)	P*Me*$_2$Ph	
cis-[Mo(*p*-TolNC)$_2$(PMe_2Ph)$_4$]	7.8—6.3m	28(28)	PMe_2*Ph* + $CNC_6H_4CH_3$	
	2.18s	6(6)	CNC_6H_4*C*H_3	
	1.64t	12(12)	*trans*-P*Me*$_2$Ph	2 X 2.4
	1.38fd	12(12)	P*Me*$_2$Ph *trans* to CNR	4.0
mer-[Mo(*p*-TolNC)$_3$(PMe_2Ph)$_3$]	7.9—6.2m	28(28)	PMe_2*Ph* + $CNC_6H_4CH_3$	
	2.04s	9(9)	CNC_6H_4*C*H_3	
	1.82t	11(12)	*trans*-P*Me*$_2$Ph	2 X 2.3
	1.78d	5(6)	P*Me*$_2$Ph *trans* to CNR	4.8
trans-[Mo(CNt-Bu)$_2$(PMe_2Ph)$_4$]	8.0—7.0m	20(20)	PMe_2*Ph*	
	1.60s	21(24)	P*Me*$_2$Ph	
	1.48s	16(18)	CNt-*Bu*	
trans-[Mo(*p*-TolNC)$_4$($PMePh_2$)$_2$]	8.0—7.0m	20(20)	$PMePh_2$	
	2.14t	5(6)	P*Me*Ph_2	2 X 2.4
	1.80s	11(12)	$CNC_6H_4CH_3$	
trans-[Mo(CNMe)$_4$($PMePh_2$)$_2$]	8.0—7.0 m	20(20)	$PMePh_2$	
	2.50s	11(12)	CN*Me*	
	2.27t	6(6)	P*Me*Ph_2	2 X 2.3

[a] In C_6D_6 at 25°C relative to internal TMS. Spectra run on a Varian EM360 spectrometer operating at 60 MHz. fd = filled-in doublet. [b] Required values in parentheses. [c] 2 X *y* values refer to virtual coupling $\lvert^2J(PH) + {}^4J(PH)\rvert$. Values reported for filled-in doublets (fd) refer to the separation between the outer lines.

TABLE 3

IR DATA FOR COMPLEXES $[M(CNR)_x(PMe_2Ph)_{6-x}]$ [a]

Complex	ν(C≡N)	$-\Delta\nu$	$-\Delta\nu/\nu$ [b]
cis-$[W(CNMe)_2(PMe_2Ph)_4]$	1815vs(br) [c]	350	0.162
trans-$[Mo(CNMe)_2(PMe_2Ph)_4]$	1780vs(br) [d]	385	0.178
mer-$[Mo(CNMe)_3(PMe_2Ph)_3]$	1950(sh), 184vs(br)	325	0.150
mer-$[Mo(p\text{-TolNC})_3(PMe_2Ph)_3]$	1950(sh), 1880vs(br)	244	0.115

[a] In C_6H_6 solution. [b] $\Delta\nu/\nu$ = [ν(C≡N)(complex) − ν(C≡N)(free isonitrile)]/ν(C≡N)(free isonitrile). [c] In THF. [d] 1782vs(br) in Nujol mull of the red isolated species.

coordination shifts also occur in the related complexes *cis*- and *trans*-$[M(CO)_4(PMe_3)_2]$ (M = Cr, Mo or W) [11].

B) Infra-red measurements

The values of ν(CN) observed for representative complexes whose configurations had been established by NMR measurements are shown in Table 3. As was observed for the complex *trans*-$[M(CNR)_2(dppe)_2]$ they show a very large decrease in the value of ν(CN) upon coordination of the isonitrile ligands ($\Delta\nu$). This predicts a similar susceptibility of the isonitrile ligands in these complexes towards attack by electrophilic reagents as has been observed for *trans*-$[M(CNR)_2(dppe)_2]$ [2,3]. Such an attack, by acids, giving rise to the formation of amines and hydrocarbons from ligating isonitriles will be described separately.

Experimental

The complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ were prepared by published methods, [12,13] as was CNMe [14] and the other isonitriles [15]. Solutions for NMR measurements were prepared under dinitrogen by adding the appropriate amount of isonitrile to a solution of a weighed quantity of the dinitrogen complex in dry, degassed $C_6{}^2H_6$ in an NMR tube. The tube was then rotated slowly and irradiated using a tungsten filament bulb (100 W) at 15 cm. Attempts to isolate solid products from such reactions by removal of solvent, or addition of precipitating solvents, gave only red oils except for *trans*-$[Mo(CNMe)_2(PMe_2Ph)_4]$ which was isolated as an impure red solid (Table 3).

^1H and ^{31}P NMR spectra were measured using a JEOL PFT 100 or Varian EM360 Instruments. Infra-red spectra were obtained using a Perkin Elmer 577 instrument.

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