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Reactions of unsaturated electrophiles with *trans*-$(PMe_3)_2Pd(Ph)(NHPh)$

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Abstract

The complex *trans*-$(PMe_3)_2Pd(Ph)(NHPh)$ (1) reacts with the unsaturated electrophiles CO_2, RNCO (R = Ph, ^{t}Bu, 2,6-^{i}PrC_6H_3), $Ph_2C{=}C{=}O$ and maleic anhydride. The less bulky substrates, CO_2 and maleic anhydride, react by net insertion into the Pd–N bond, while the bulky electrophiles ^{t}BuNCO, (2,6-^{i}Pr-C_6H_3) NCO, and $Ph_2C{=}C{=}O$ react by N–H addition. ^{15}N labeling experiments show that the initial product of the reaction of phenylisocyanate with **1** is the Pd–N insertion product which then tautomerizes to the N–H addition product.

Key words: Palladium; Unsaturated electrophiles

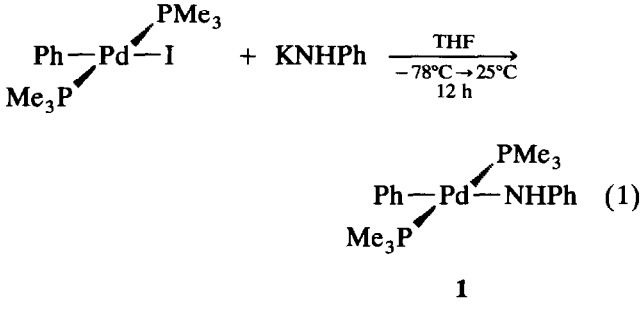
1. Introduction

There has been a growing interest in the synthesis of late transition metal amide complexes [1]. One goal of these studies has been to define the reactivity of the $M–NR_2$ group with unsaturated organic compounds. Of particular interest is the determination of whether or not $M–NR_2$ complexes can mediate C–N bond forming reactions that are similar to the C–C bond forming reactions mediated by metal alkyl complexes. Recent interest in this chemistry has resulted in the synthesis of a variety of new metal amide complexes [2], and the emergence of the reactivity patterns of these compounds [3]. In particular, metal amide complexes have been shown to undergo insertion or addition reactions with CO_2, RNCO and CO [4]. This paper describes the synthesis of the anilide complex *trans*-$(PMe_3)_2Pd(Ph)(NHPh)$ (**1**) and its reactions with the unsaturated electrophiles CO_2, RNCO, $Ph_2C{=}C{=}O$, and maleic anhydride.

2. Results

2.1. Preparation and characterization of *trans*-$(PMe_3)_2Pd(Ph(NHPh)$ (1)

The anilide complex *trans*-$(PMe_3)_2Pd(Ph)(NHPh)$ (**1**) was prepared by the reaction of *trans*-$(PMe_3)_2$-Pd(Ph)I with KNHPh in THF at room temperature (eqn. (1)).



(1)

1

Removal of the THF under reduced pressure and recrystallization of the resultant brown oil from diethyl ether at 0°C affords compound **1** as yellow crystals in 53% yield. Compound **1** is air sensitive in solution and in the solid state, but is stable under an argon atmosphere at room temperature. It slowly decomposes when heated to > 90°C by losing phosphine and dimerizing (the chemistry associated with dimerization and subsequent reductive elimination will be reported separately).

The ^1H NMR spectrum of **1** in C_6D_6 reveals a triplet at 0.74 ppm for the protons of PMe_3, a broad singlet at 1.66 ppm for the N–H proton, and three well defined peaks in the phenyl region. The $^{31}P\{^1H\}$ NMR spectrum reveals a singlet at −16.79 ppm, consistent with the presence of *trans* phosphine ligands. The

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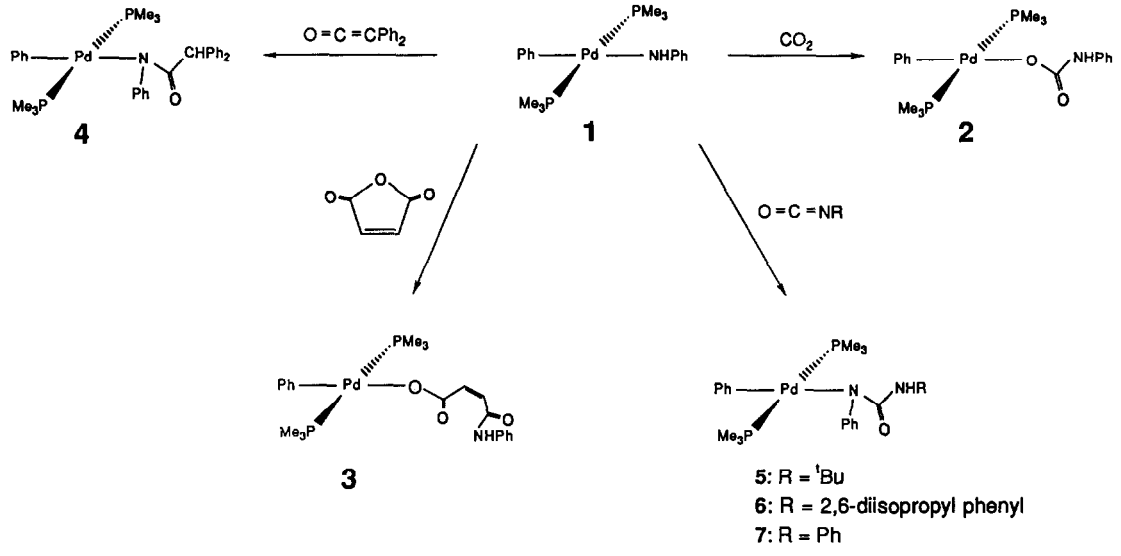


Scheme 1.

$^{13}C\{^1H\}$ NMR spectrum of **1** exhibits a triplet at 157.2 ppm ($^2J(^{31}P-^{13}C) = 12$ Hz) which is assigned to the *ipso*-phenyl carbon that is *trans* to the anilide group. The ^1H NMR spectrum of *trans*-$(PMe_3)_2Pd(Ph)(^{15}NHPh)$ (**1**-^{15}N) has a doublet at 1.66 ppm ($^1J(H-^{15}N) = 69$ Hz) further confirming the assignment of the spectrum of **1**. Although the value of $^1J(H-^{15}N)$ would seem to indicate sp^3 hydridization at nitrogen, this coupling constant is similar to the value of 71 Hz found in *trans*-$(PEt_3)_2Pt(H)(NHPh)$. A low temperature X-ray diffraction study of the Pt complex revealed a planar geometry around the anilide nitrogen [4a]. Thus compound **1** appears to have an analogous structure [4d]. The $^{31}P\{^1H\}$ NMR spectrum of **1**-^{15}N consists of a singlet at -16.8 ppm. The small $^2J(^{31}P-^{15}N)$ coupling constant (< 3 Hz) is consistent with both phosphine ligands being *cis* to the anilide group [4a].

2.2. Reaction chemistry of 1 with electrophiles

A suspension of complex **1** in pentane reacts with CO_2 (1 atm, 25°C) to afford a white precipitate of the phenyl carbamate complex **2** in 82% yield (Scheme 1). The IR spectrum reveals ν(C=O) at 1630 cm^{-1}, while a resonance in the $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$ at 158.8 ppm is assigned to the carbonyl carbon [4d*]. The ^1H NMR spectrum of **2** in C_6D_6 reveals the loss of the N–H singlet at 1.66 ppm and the appearance of a new singlet at 8.51 ppm which is assigned to the N–H of the carbamate.

Reaction of **1** with maleic anhydride in pentane affords the Pd–N insertion product *trans*-$(PMe_3)_2Pd(Ph)[OC(O)CHCHC(O)NH)Ph)]$ (**3**) as a beige solid (Scheme 1). The ^1H NMR spectrum of **3** in C_6D_6 reveals a broad singlet at 14.06 ppm for the N–*H* proton and two singlets at 6.34 and 6.36 ppm for the alkene protons, which appear as an AB quartet in d_8-toluene. In the $^{13}C\{^1H\}$ NMR spectrum of **3**, there are two singlets at 170.8 and 163.3 ppm for the carbonyl carbons and a triplet at 135.9 ppm (J(P–C) = 5 Hz) for the α-alkene carbon. Compound **3** was also characterized by its IR spectrum (ν(NH) = 2731 cm^{-1}, ν(CO) = 1671 cm^{-1}, ν(CO) = 1621 cm^{-1}, ν(C=C) = 1589 cm^{-1}). The ^1H NMR spectrum of **3**-^{15}N (formed by reaction of **1**-^{15}N with maleic anhydride) has a doublet at 14.1 ppm ($^1J(H-^{15}N) = 70$ Hz) confirming that the proton remains bonded to the ^{15}N in **3**-^{15}N. The absence of non-PMe_3 aliphatic carbon peaks in the ^{13}C NMR spectrum of **3** rules out insertion of the C=C double bond of maleic anhydride into the N–H or N–M bond. The structure proposed for **3** in Scheme 1 is similar to the structures of the products of the reaction of Ir [8a] or Re [8b] alkoxides with maleic anhydride.

When **1** was allowed to react with diphenyl ketene in pentane, the N–H addition product **4** was generated as a white solid (Scheme 1). The ^1H NMR spectrum of **4** reveals the appearance of a new broad singlet at 6.06 ppm. The ^1H NMR of **4**-^{15}N shows that there is loss of the ^{15}N–H coupling and that the singlet at 6.06 ppm is the C–H proton of **3**-^{15}N. A C=O stretching absorption at 1598 cm^{-1} is also observed as well as a resonance in the $^{13}C\{^1H\}$ NMR spectrum of **4** at 174.1 ppm for the

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

carbonyl carbon and a singlet at 62.8 ppm for the α-keto carbon. Once again, the *trans* stereochemistry at the metal center is preserved with the presence of a singlet at −18.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The formation of **4** can be explained by the addition of the N–H bond of **1** across the carbon–carbon double bond of diphenyl ketene. In this reaction, complex **1** reacts with diphenyl ketene in a fashion similar to a 2° amine [5].

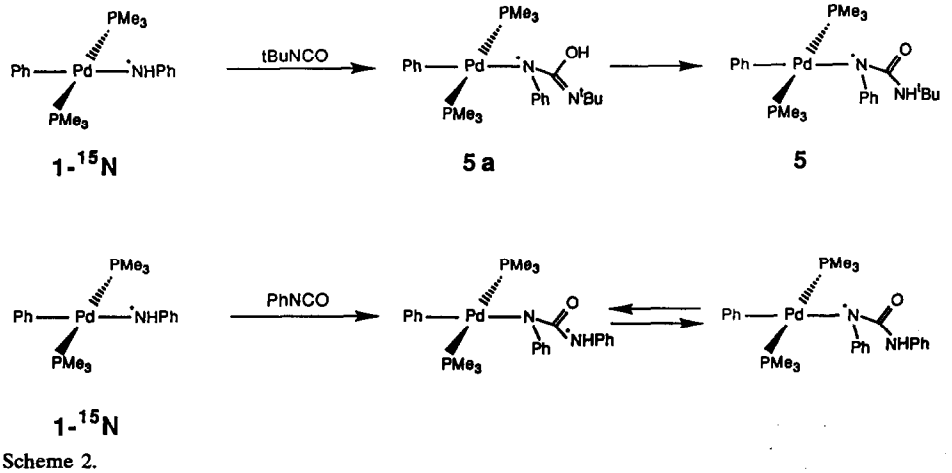
Compound **1** also reacts with a variety of alkyl and aryl isocyanates. The reaction of one equivalent of tert-butyl isocyanate with **1** in pentane at room temperature generates the N–H addition product *trans*-$(PMe_3)_2Pd(Ph)[N(Ph)C(O)NH^tBu]$ (**5**) as a white solid. The emergence of a broad singlet at 5.44 ppm in the ^1H NMR spectrum arising from the N–H proton as well as a singlet at 161.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum for the carbonyl carbon and a C=O stretch at 1616 cm^{-1} supports the formation of **5** [3d,5a,b]. To confirm that **5** results from the addition of the N–H bond to t-BuNCO, t-BuNCO was allowed to react with **1**-^{15}N in C_6D_6. The ^1H NMR spectrum of the reaction mixture reveals the same broad singlet at 5.44 ppm with no indication of ^{15}N–H coupling. This observation is consistent with the formation of **5** by net addition of the N–H bond across the N–C bond of the isocyanate.

When **1**-^{15}N was allowed to react with ^{t}Bu-NCO at −60°C in d_8-toluene in a ^1H NMR spectrometer, no reaction was observed. Warming this sample to 0°C showed the formation of a new product, **5a**, with a singlet at 7.34 ppm. We believe that this compound is the O protonated tautomer of **5** (Scheme 2). The sample was then warmed to room temperature whereupon **5a** converted to **5** over a period of twelve hours.

In a procedure identical to that of the reaction of **1** with tert-butyl isocyanate, 2,6-diisopropylphenyl isocyanate was reacted with **1** to generate the addition product, **6**, (Scheme 1). Once again, the presence of a singlet at 160.0 ppm in the $^{13}C\{^1H\}$ NMR spectrum for the carbonyl carbon as well as a C=O stretch at 1619 cm^{-1} confirms formation of the addition product, **6** [3d,5a,b]. The N–H proton could not be located in the ^1H NMR of **6** due to the complicated phenyl region, but the N–H stretch was observed in the IR spectrum (ν(N–H) = 3337 cm^{-1}). Although our inability to find the N–H resonance in the ^1H NMR spectrum prohibits unambiguous ^{15}N-labeling experiments, it is believed that **1** behaves like an organic amine.

Similar reaction chemistry was observed when **1** was allowed to react with phenyl isocyanate. The addition of one equivalent of phenyl isocyanate to a solution of **1** in pentane at room temperature affords the addition product **7** as a white solid (Scheme 1). The ^1H NMR of **7** reveals a singlet at 7.86 ppm, which has been assigned to the N–H proton of the carbamate complex **7**. The $^{13}C\{^1H\}$ NMR spectrum reveals a singlet at 158.6 ppm, which is consistent with the carbonyl carbon as well as a C=O stretching absorption at 1627 cm^{-1} in the IR spectrum. All other spectroscopic data were consistent with the addition product **7**.

In order to determine whether the complex **7** was generated by the insertion of PhNCO into the Pd–N bond or by the direct addition of the NH bond of **1** to PhNCO, the reaction of **1**-^{15}N with PhNCO was performed in d_8-toluene and monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum at 20°C reveals a triplet at 7.86 ppm. Upon closer examination, the triplet is best assigned to a 1:1 mixture of ^{14}N–H and ^{15}N–H (J(N–H) = 82 Hz) isotopomers which arise from a statistical distribution of ^{15}N between the two N sites at 20°C (Scheme 2). The addition of PhNCO to **1**-^{15}N was then monitored at −60°C. The ^1H NMR spectrum at



Scheme 2.

−60°C reveals that the initial product is the insertion product which produces a doublet at 7.86 ppm. Upon warming from −60°C to 20°C, the ^{14}N singlet grows in until a statistical distribution is reached. The ^{15}N-labeling studies suggest that the initial species generated is the insertion product which then tautomerizes to the

TABLE 1. ^1H NMR spectroscopic data [a]

Compound	δ, ppm	multiplicity	J, Hz	integral	assignment
trans-$(Me_3P)_3Pd(C_6H_5)(NHPh)$ (1) [b]	0.74	t	3	18	*trans*-PMe_3
	1.66	s		1	-N-H
	6.53	t	7	1	aromatic
	6.80	d	8	2	"
	6.97	t	7	1	"
	7.10	t	7.4	2	"
	7.28	t	7.3	2	"
	7.37	d	7.4	2	"
trans-$(Me_3P)_2Pd(C_6H_5)[(OC(O)NHPh)]$ (2) [c]	1.13	t	3.3	18	*trans*-PMe_3
	6.88	t	7.8	2	aromatic
	7.00	t	8.6	2	"
	7.27	m		3	"
	7.33	d	7.3	2	"
	7.64	d	8.1	2	"
trans-$(Me_3P)_2Pd(C_6H_5)[OC(O)CHCH(O)NH(Ph]$ (3) [b]	0.68	s		18	*trans*-PMe_3
	6.35	s		1	-C=C*H*
	6.36	s		1	-C=C*H*
	6.89	t	6.6	2	aromatic
	6.96	t	10	2	"
	7.24	m		4	"
	8.31	d	7.7	2	"
	14.06	s		1	N*H*Ph
trans-$(Me_3P)_2Pd(C_6H_5)[N(Ph)C(O)CHPh_2]$ (4) [c]	0.82	t	3.4	18	*trans*-PMe_3
	6.07	s		1	C-H
	6.88	t	7.0	1	aromatic
	6.99	t	7.3	1	
	7.08	t	7.7	1	
	7.28	m			
	7.48	d	~0	1	
	7.63	d	8.1	1	
	7.7	d		4	
trans-$(Me_3P)_2Pd(C_6H_5)[N(Ph)C(O)NH^tBu]$ (5) [b]	0.69	t	3.7	18	*trans*-PMe_3
	1.58	s		9	$C(CH_3)_3$
	5.44	s		1	-N-H
	6.73	t	7		aromatic
	7.03	m		3	"
	7.25	m		2	"
	7.40	t	7	2	"
	8.45	d	8.5	2	"
trans-$(Me_3P)_2Pd(C_6H_5)[N(Ph)C(O)NHAr)$ (6) [b]	0.76	t	3.5		*trans*-PMe_3
	1.35	d	6.8		$CH(CH_3)_2$
	3.64	m			$CH(CH_3)_2$
	6.92	m			
	7.01	t	7.5		aromatic
	7.25	m			"
	7.36	t	7.5		"
	8.41	d	8.		"
trans-$(Me_3P)_2Pd(C_6H_5)[N(Ph)C(O)NHPh]$ (7) [b]	0.60	t	3.5	18	*trans*-PMe_3
	6.92	m		2	aromatic
	7.27	t	3	2	"
	7.38	t	3	2	"
	7.91	s		1	-N-H
	8.06	d	9.8	2	aromatic
	8.46	d	8.5	2	"

[a] All spectroscopic data were collected at 23°C. [b] C_6D_6. [c] $CDCl_3$. [d] The multiplicity doublet and triplet are apparent splitting patterns when referring to the PMe_3 ligands and do not necessarily reflect the true coupling constants.

^{14}N–^{15}N isotopic regioisomers (Scheme 2). These findings are consistent with Trogler's mechanistic investigations of PhNCO insertion into a Pt–N bond [4a].

The results of the reactions between **1**-^{15}N and the substrates CO_2, PhNCO, and maleic anhydride show that insertion of the substrate into the Pd–N bond is

TABLE 2. $^{13}C\{^1H\}$ NMR spectroscopic data [a]

Compound	δ, ppm	multiplicity	J, Hz	assignment
trans-$(Me_3P)_2Pd(C_6H_5)(NHPh)$ (**1**) [b]	12.9	t	13.5	*trans*-PMe_3
	108.5	s		aromatic
	108.6	s		
	151.1	s		
	115.2	s		
	122.1	s		
	129.0	s		
	129.2	s		
	135.9	s		
	137.0	s		
	157.1	t	12.2	Pd–C
	162.2	s		
trans-$(Me_3P)_2Pd(C_6H_5)[OC(O)NHPh]$ (**2**) [c]	12.5	t	14	*trans*-PMe_3
	116.9	s		aromatic
	119.8	s		
	122.2	s		
	127.2	s		
	128.3	s		
	135.7	t	4.8	
	142.0	s		
	148.4	t	12	Pd–C
	158.9	s		C=O
trans-$(Me_3P)_2Pd(C_6H_5)[OC(O)CHCH(O)NH(Ph)]$ (**3**) [b]	12.2	t	14.3	*trans*-PMe_3
	119.6	s		aromatic
	122.9	s		(H)C=*C*(H)–C(O)–N(H)Ph
	123.1	s		
	127.6	s		
	128.9	s		
	133.4	s		
	134.5	s		
	135.9	t	4.8	Pd–O–L(O)–*C*(H)
	140.5	s		
	149.1	t	7.9	Pd–C
	163.3	s		C=O
	171.6	s		C=O
trans-$(Me_3P)_2Pd(C_6H_5)[N(Ph)C(O)CHPh_2]$ (**4**) [c]	12.9	t	14.7	*trans*-PMe_3
	62.8	s		*C*–H
	120.6	s		aromatic
	122.8	s		
	123.9	s		
	126.0	s		
	127.2	s		
	127.6	s		
	127.7	s		
	128.0	s		
	128.3	s		
	128.7	s		
	128.8	s		
	129.3	s		
	136.6	s		
	137.2	s		
	143.0	s		
	150.9	s		
	151.5	t	9.0	Pd–C
	174.1	s		C=O

TABLE 2 (continued)

Compound	δ, ppm	multiplicity	J, Hz	assignment
trans-$(Me_3P)_2Pd(C_6H_5)$[N(Ph)C(O)NH^{t}Bu (**5**) [b]	12.9	t	14.5	*trans*-PMe_3
	30.2	s		$-C(CH_3)_3$
	49.5	s		$-C(CH_3)_3$
	117.2	s		aromatic
	117.6	s		
	122.0	s		
	122.8	s		
	136.5	s		
	137.0	s		
	153.5	s		
	154.2	t	9.0	Pd–C
	161.2	s		C=O
trans-$(Me_3P)_2Pd(C_6H_5)$[N(Ph)C(O)NHAr] (**6**) [b]	12.7	t	14.7	*trans*-PMe_3
	24.3	s		$-CH(CH_3)_2$
	28.8	s		$-CH(CH_3)_2$
	118.5	s		aromatic
	122.7	s		
	122.9	s		
	123.2	s		
	126.0	s		
	128.4	s		
	135.1	s		
	137.0	s		
	145.6	s		
	154.2	t	8.8	Pd–C
	154.7	s		
trans-$(Me_3P)_2Pd(C_6H_5)$[N(Ph)C(O)NHPh] (**7**) [b]	12.53	t	14.7	*trans*-PMe_3
	117.3	s		aromatic
	118.9	s		
	120.5	s		
	122.7	s		
	123.0	s		
	129.1	s		
	136.3	s		
	137.0	s		
	142.8	s		
	152.4	s		
	153.3	t	8.8	Pd–C
	158.6	s		C=O

[a] All spectroscopic data were collected at 23°C. [b] C_6D_6. [c] $CDCl_3$.

the preferred mode of reaction. When the bulky electrophiles Ph_2CCO, ^{t}Bu-NCO and (2,6-$(^i Pr)_2C_6H_3$)NCO react with **1**, complex **1** behaves as an organic amine with net addition of the NH bond to the electrophile. The results of all these experiments are consistent with a mechanism of reaction that involves initial nucleophilic attack of the anilide group at the most electrophilic carbon atom of the substrate followed by transfer of the proton or Pd group to the substrate. It appears as though steric considerations control the partitioning of the substrates between Pd–N insertion and N–H addition products, with N–H addition being favored with bulky electrophiles.

These studies are consistent with the findings of other work on the insertion chemistry of late transition metal amide complexes, and show that the chemistry is dominated by the nucleophilicity of the amide lone pair of electrons. Direct attack of the amide lone pair on the electrophile appears to be the preferred mode of reaction. This mode of reaction can be further modified by the steric demands of the substrate and the presence of atoms that can coordinate to the metal center. If it is true that the lone pair is always involved in the insertion chemistry of the amide group, then serious questions are raised about the ability of compounds such as **1** to undergo insertion reactions with unactivated substrates.

3. Experimental section

All procedures were carried out under an atmosphere of argon using standard Schlenk techniques.

TABLE 3. $^{31}P\{^1H\}$ NMR spectroscopic data [a]

Compound	δ, ppm	Mult.
1 [b]	−16.79	s
2 [c]	−16.22	s
3 [b]	−17.46	s
4 [c]	−18.40	s
5 [b]	−17.07	s
6 [b]	−17.66	s
7 [b]	−17.27	s

[a] All spectroscopic data were collected at 23°C. [b] C_6D_6. [c] $CDCl_3$.

The compound *trans*-$(Me_3P)_2Pd(C_6H_5)$ **1** was prepared by literature procedures [6]. Maleic anhydride, t-butyl isocyanate, phenyl isocyanate, and 2,6-diisopropyl isocyanate were purchased from Aldrich. Diphenyl ketene was prepared by literature procedures [7]. Solvents and reagents were dried and deoxygenated by using standard methods prior to use. KNHPh and $K^{15}NHPh$ were prepared by the reaction of the respective aniline and KH in THF. NMR spectra were obtained on either General Electric QE-300 or Varian VXR 300 spectrometers. Proton of carbon NMR chemical shifts were referenced to residual signals in the solvent and are reported relative to TMS. ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Infrared data were collected on a Perkin-Elmer 1600 spectrometer. High resolution mass spectra were measured using chemical ionization with methane as the reactant gas.

3.1. Preparation of trans-$(Me_3P)_2Pd(C_6H_5)(NHPh)$ (1)

A solution of *trans*-$(Me_3P)_2Pd(C_6H_5)I$ (278 mg, 0.600 mmol) in 20 ml of THF was cooled to −78°C. To this solution was added KNHPh (118 mg, 0.900 mmol) as a solution of THF. Once all the amide was added, the reaction mixture was warmed to room temperature and stirred for 12 h. The solution was a deep orange-red with a very fine suspended solid. The solvent was removed under reduced pressure, and the residue was extracted with diethyl ether (2 × 15 ml). The combined extracts were filtered, concentrated to *ca.* 10 ml, and cooled to −78°C to afford pale yellow crystals of **1** (135 mg); yield 52.6%. IR (Nujol, cm^{-1}): 3327 (N–H). Anal. Calcd. for $C_{18}H_{29}NP_2Pd$: C, 50.54, H. 6.79; N, 3.28. Found: C, 49.81; H, 6.90; N, 3.21%.

3.2. Reaction of 1 with carbon dioxide

Carbon dioxide gas was bubbled into a pale yellow solution of **1** (139 mg; 0.325 mmol) in 10 ml of pentane for 5 min. During this time, a white-yellow precipitate formed. The solution was allowed to stir for 12 h at room temperature under a CO_2 atmosphere. Solvent was removed under reduced pressure to afford 125 mg of **2** (81.6%). Recrystallization of **2** in diethyl ether at 0°C afforded white crystals suitable for analysis. IR (KBr, cm^{-1}): 3286 [ν(N–H)], 1630 [ν(C=O)]. Anal. Calcd. for $C_{19}H_{29}NO_2P_2Pd$: C, 48.37; H, 6.15; N, 2.97. Found: C, 48.32; H, 6.24; N, 2.93%.

3.3. Reaction of 1 with maleic anhydride. Synthesis of trans-$(PMe_3)_2Pd(C_6H_5)[OC(O)C(H)C(H)C(O)NHPh]$ (3)

To a solution of **1** (86 mg; 0.200 mmol) in pentane (15 ml) was added 1:1 equiv of maleic anhydride (22 mg; 0.220 mmol). The solution was allowed to stir for 12 h at room temperature, during which time a white precipitate formed. The white precipitate was isolated by filtration and washed with 5 ml of pentane to give 73 mg of crude product (**3**) (69.5%). Recrystallization of **3** in diethyl ether at 0°C produced white microcrystals suitable for elemental analysis. IR (KBr, cm^{-1}): 2731 (ν(N–H), 1670 [ν(C=O)], 1621 [ν(C=O)], 1589 [ν(C=C)]. Anal. Calcd. for $C_{22}H_{31}NO_3P_2Pd$: C, 50.24; H, 5.90; N, 2.66. Found: C, 50.01; H, 5.89; N, 2.64%.

3.4. Reaction of 1 with diphenyl ketene. Synthesis of trans-$(PMe_3)_2Pd(C_6H_5)[N(Ph)C(O)C(H)Ph_2]$ (4)

Excess diphenyl ketene (0.2 ml) was added to a solution of **1** (136 mg; 0.318 mmol) in pentane (15 ml). Immediate formation of a pale yellow precipitate was observed. The solution was allowed to stir for 12 h at room temperature. The precipite was isolated by filtration to give 135 mg of crude product (**4**) (68.3%). Recrystallization of **4** from diethyl ether at 0°C afforded white microcrystals suitable for elemental analysis. IR (KBr, cm^{-1}): 1598 [ν(C=O)]. High Res. M.S. Calcd. for $C_{32}H_{39}NOP_2Pd$: 621.1666. Found: 621.1620.

3.5. Reaction of 1 with t-butyl isocyanate. Synthesis of trans-$(PMe_3)_2Pd(C_6H_5)[N(Ph)C(O)NH(^tBu)]$ (5)

t-Butyl isocyanate (38 μl; 0.334 mmol) was added to a solution of **1** (103 mg; 0.223 mmol) in pentane *ca.* 10 ml. A white precipitate formed upon stirring for 12 h. Isolation of the white solid by filtration afforded 89 mg of **5** (75.8%). Recrystallization of **5** in diethyl ether at 0°C gave white microcrystals suitable for analysis. IR (KBr, cm^{-1}): 3334 [ν(N–H)], 1616 [ν(C=O)]. High Res. M.S. Calcd. for $C_{23}H_{38}N_2OP_2Pd$: 526.1493. Found: 526.1509.

3.6. Reaction of 1 with 2,6-diisopropylphenyl isocyanate. Synthesis of trans-$(PMe_3)_2Pd(C_6H_5)[N(Ph)C(O)NH2,6-(^iPr)_2(C_6H_3)]$ (6)

2,6-Diisopropylphenyl isocyanate (71 μl; 0.333 mmol) was added to a solution of **1** (95 mg; 0.222 mmol) in pentane *ca.* 10 ml. A white precipitate formed upon stirring for 12 h. Isolation of the white solid by

filtration afforded 93 mg of **6** (67.7%). Recrystallization in diethyl ether at 0°C afforded white microcrystals of **6**. IR (KBr, cm^{-1}): 3337 [ν(N–H)], 1619 [ν(C=O)].

3.7. Reaction of 1 with phenyl isocyanate. Synthesis of trans-$(PMe_3)_2Pd(C_6H_5)[N(Ph)C(O)NHPh]$ (7)

Phenyl isocyanate (22 μl; 0.201 mmol) was added to a solution of **1** (86 mg; 0.201 mmol) in pentane *ca.* 10 ml. A white precipitate formed upon stirring for 12 h. Isolation of the white solid by filtration afforded 50 mg of **7** (45.5%). IR (KBr, cm^{-1}): 3318 [ν(N–H)], 1627 [ν(C=O)]. High Res. M.S. Calcd. for $C_{25}H_{34}N_2OP_2Pd$: 546.1180. Found: 546.1203.

3.8. Synthesis of ^{15}N-labeled compounds

(a) *trans*-$(PMe_3)_2PdPh(^{15}NHPh)$ **1**-^{15}N was synthesized following the same procedure for **1** using *trans*-$(PMe_3)_2Pd(Ph)I$ and $K^{15}NHPh$. ^1H NMR (C_6D_6): δ 1.66 ppm (J(N–H) = 69 Hz).

(b) Following the same procedure for **3**, **4** and **5**, **1**-^{15}N was reacted with maleic anhydride, diphenyl ketene and t-butyl isocyanate to generate **3**-^{15}N, **4**-^{15}N and **5**-^{15}N respectively.

(c) In an NMR tube, a solution of **1**-^{15}N (20 mg; 0.05 mmol) in 0.5 ml of d_8-toluene was prepared and cooled to −78°C. To this solution, 1 equiv of diphenyl ketene was added (10 mg). The reaction was monitored by ^1H NMR spectroscopy at 20° integrals between the temperature range of −60°C to 20°C.

(d) In an NMR tube, a solution of **1**-^{15}N (17 mg; 0.04 mmol) in 0.5 ml of d_8-toluene was prepared and cooled to −78°C. To this solution, 1 equiv of tert-butyl isocyanate was added (4.5 μl). The reaction was monitored by ^1H NMR spectroscopy at 20° integrals between the temperature range −60°C to 20°C.

(e) In an NMR tube, a solution of **1**-^{15}N (25 mg; 0.06 mmol) in 0.5 ml of d_8-toluene was prepared and cooled to −78°. To this solution, 1 equiv of phenyl isocyanate was added (6 μl). The reaction was monitored by ^1H NMR spectroscopy at 20° integrals between the temperature range of −60°C to 20°C.

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