Synthesis, Characterization, and Reactivity of *trans*-Ir$(PR_3)_2$(CO)(NHR′), Where R = Me and Et and R′ = Ph and Bu^t

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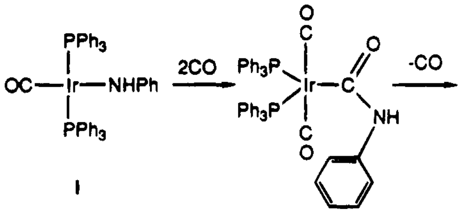
The synthesis and characterization of terminal Ir(I)-amido complexes containing trialkylphosphine ligands are described. The anilide complexes, *trans*-Ir$(PR_3)_2$(CO)(NHPh), where PR_3 = PMe_3 (**1**) and PEt_3 (**2**), undergo insertion reactions with CO and subsequent C-H activation to produce $\overline{Ir(PR_3)_2(CO)(H)[C(O)NH(C}_6H_4)]$, **5** and **6**. The structure of these orthometallated products is similar to that found for the analogous PPh_3 complexes reported previously. It was also possible for the first time to synthesize an alkylamide complex, *trans*-Ir$(PEt_3)_2$(CO)(NHBu^t), **3**, which was found to readily convert to an amido-bridged dimeric species [Ir(PEt_3)(CO)(μ-NHBu^t)]$_2$, **4**. A rapid reaction results between **3** and CO to produce a carbamoyl complex, Ir$(PEt_3)_2(CO)_2$[C(O)NHBu^t], **7**. A detailed spectroscopic study established the structure of **7** to be trigonal bipyramidal, with the carbamoyl ligand in an axial position and the phosphine ligands distributed between axial and equatorial positions. An alkyne adduct was formed between **3** and PhC≡CPh, whereas PhC≡CH produces a monoalkynyl complex. Addition of two or more equivalents of PhC≡CH ultimately affords the bisalkynyl complex, *trans*-Ir$(PEt_3)_2$(CO)(H)(-C≡CPh)$_2$, **9**.

Introduction

Amido (NHR$^-$ or NR$_2^-$) groups are widely used in coordination and organometallic chemistry as π-electron donating coligands for middle to early transition metals.[1] Interest in late transition metal amido complexes has been growing lately,[2–7] because the amido ligands in these complexes are expected to be reactive due to the lack of ligand-to-metal π bonding. We have begun a study of low-valent group 9 metal-amide complexes, and have recently reported the synthesis of *trans*-Ir$(PPh_3)_2$(CO)(NHAr) complexes, where Ar = C_6H_5, *o*-C_6H_4-Me, *p*-C_6H_4Me, 2,6-$C_6H_3Me_2$, 3,5-$C_6H_3Me_2$, *p*-$C_6H_4NO_2$ and *p*-C_6H_4Cl.[7] Most interestingly, these complexes, except the one bearing the NH(*p*-$C_6H_4NO_2$) ligand, undergo facile insertion of CO, which is a key step in metal-assisted functionalization of amines and amides for synthetic purposes. For the complexes containing the bulky -NH(2,6-$C_6H_3Me_2$) and -NH(3,5-$C_6H_3Me_2$) ligands, the insertion reaction results in the formation of carbamoyl (-C(O)NHAr) moieties. For the other complexes, the insertion reaction is followed by orthometallation of the carbamoyl moiety:



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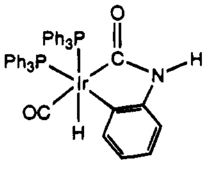

III

Such unprecedented intramolecular C-H bond activation of a carbamoyl ligand prompted us to examine this reaction for other complexes that are structurally similar but have phosphine coligands with different steric and electronic properties. In this regard, we report here the synthesis and characterization of complexes containing trialkylphosphine ligands, viz. *trans*-

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[1] For a review of early transition metal amido complexes, see: Chisholm, M. H.; Rothwell, I. P. in *Comprehensive Coordination Chemistry*; Wilkinson, G. Ed.; Pergamon Press; Oxford, England, 1987, Vol. 2, p 161.

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Ir(PR$_3$)$_2$(CO)(NHPh), where PR$_3$ = PMe$_3$ and PEt$_3$. We also report the first example of an Ir(I)-*alkyl*amide complex, *trans*-Ir(PEt$_3$)$_2$(CO)(NHBu^t). Reactions of these complexes with CO and alkynes are discussed.

Experimental Section

All preparations were carried out under N$_2$ using standard drybox or Schlenk line techniques. Solvents were purified twice before use and stored under N$_2$ over 4-Å molecular sieves. Hexanes and pentane were distilled from CaH$_2$, and toluene and THF were distilled from Na/K alloy and benzophenone. LiNHPh and LiNH^{t}Bu were prepared by reacting the corresponding amines with ^{n}BuLi in toluene. *trans*-Ir(PR$_3$)$_2$(CO)-Cl [PR$_3$ = PMe$_3$ and PEt$_3$] were prepared by a method developed in our laboratory.[8]

Infrared spectra were recorded on either a Nicolet 6000 or a Mattson Galaxy FT-IR instrument. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained using either a 250- or a 500-MHz Bruker instrument. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were dried over 4-Å molecular sieves. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses. *trans*-Ir(PR$_3$)$_2$(CO)(NHPh) (PR$_3$ = PMe$_3$ (1), and PEt$_3$ (2)). Both of these complexes were prepared by dissolving *trans*-Ir(PR$_3$)$_2$(CO)Cl in THF and adding 3 equiv of LiNHPh, also dissolved in THF. The resulting bright yellow solutions were allowed to stir at room temperature for 10 min, after which time they were evacuated to dryness. The gummy brown solid residues were then extracted with hexane and filtered through a half-inch pad of Celite to give clear yellow solutions. Concentration of the hexane solutions under vacuum and cooling to −10 °C for 12 h yielded bright yellow microcrystalline solids, which were separated by filtration. Further concentration of the filtrate and cooling to −10 °C gave a second crop of solids. Combined yields were ~75%. **1.** Found: C, 33.1; H, 4.9; N, 3.1. Calc.: C, 33.6; H, 5.2; N, 3.0. IR (carbonyl region), THF, cm^{-1}: 1935. ^{1}H NMR, C$_6$D$_6$: δ 7.18 (t, J_{H-H} = 8.5 Hz, 2H), 6.71 (d, J_{H-H} = 8.0 Hz, 2H), 6.55 (t, J_{H-H} = 8.0 Hz, 1H) (C$_6$*H*$_5$); 2.43 (s, 1H, N*H*C$_6$H$_5$); 1.11 (t, 18H, PC*H*$_3$). ^{13}C{^{1}H} NMR, C$_6$D$_6$: δ 173.8 (t, J_{P-C} = 12 Hz, Ir-*CO*). ^{31}P{^{1}H} NMR, C$_6$D$_6$ (referenced against external H$_3$PO$_4$ standard): δ −20.0. **2.** Found: C, 41.5; H, 6.7; N, 2.4. Calc.: C, 41.6; H, 6.6; N, 2.5. IR (carbonyl region), THF, cm^{-1}: 1931. ^{1}H NMR, C$_6$D$_6$: δ 7.20 (t, J_{H-H} = 8.0 Hz, 2H), 6.70 (d, J_{H-H} = 8.2 Hz, 2H), 6.57 (t, J_{H-H} = 8.0 Hz, 1H) (C$_6$*H*$_5$); 2.26 (s, 1H, N*H*C$_6$H$_5$); 1.65 (m, 12H, PC*H*$_2$CH$_3$); 0.95 (m, 18H, PCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR, C$_6$D$_6$: δ 173.2 (t, J_{P-C} = 14 Hz, Ir-*CO*). ^{31}P{^{1}H} NMR, C$_6$D$_6$ (referenced against external H$_3$PO$_4$ standard): δ 18.7.

***trans*-Ir(PEt$_3$)$_2$(CO)(NHBu^t), 3.** In a typical preparation, *trans*-Ir(PEt$_3$)$_2$(CO)Cl (0.05 g, 0.1 mmol) was dissolved in C$_6$H$_6$ (3 mL) and a solution (C$_6$H$_6$, 2 mL) of LiNHBu^t (0.01 g, 0.1 mmol) was added to it. The mixture was stirred for 2.5 h, during which time the clear solution gradually turned cloudy. At the end of this period, the cloudy mixture was filtered through Celite to give a clear yellow solution containing *trans*-Ir(PEt$_3$)$_2$(CO)(NHBu^t) in 99% purity (by NMR). Any attempt to isolate the complex by concentrating the solution always resulted in its conversion to a dimeric complex, discussed below. Therefore, characterization of **3** was based on its spectroscopic analysis in solution. IR (carbonyl region), C$_6$H$_6$, cm^{-1}: 1905. ^{1}H NMR, C$_6$D$_6$: δ 1.80 (m, 12H, PC*H*$_2$CH$_3$); 1.68 (s, 1H, N*H*C(CH$_3$)$_3$); 1.41 (s, 9H, NHC(C*H*$_3$)$_3$); 1.01 (q, 18H, PCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR, C$_6$D$_6$: δ 142.9 (t, J_{P-C} = 6.5 Hz). ^{31}P{^{1}H} NMR, C$_6$D$_6$: δ 13.4.

[Ir(PEt$_3$)(CO)(μ-NHBu^t)]$_2$, 4. A solution of complex **3** (0.10 g, 0.19 mmol) in benzene (10 mL) was sealed in a glass ampule under vacuum and was heated at 80 °C, resulting in the yellow color of the solution to gradually change to bright orange. Although reaction appeared complete after ca. 6 h, the ampule was heated for 12 h to ensure completion, after which time the ampule was taken inside an inert atmosphere glove-box, the seal was broken and the content was transferred into a Schlenk flask. The volatiles were then removed under vacuum for 12 h to ensure complete removal of free PEt$_3$. The resulting dark orange waxy solid was dissolved in a minimum volume of pentane, and the solution was cooled to −78 °C for ca. 10 h to precipitate [Ir(PEt$_3$)(CO)(μ-NHBu^t)]$_2$ as dark orange microcrystalline solids. The yield was 30%. Found: C, 31.8; H, 6.4; N, 3.2. Calc.: C, 32.1; H, 6.1; N, 3.4. IR, C$_6$H$_{14}$, cm^{-1}: 1931 and 1912. ^{1}H NMR, C$_6$D$_6$: δ 3.25 (t, J_{P-H} = 3 Hz, 1H, N*H*C(CH$_3$)$_3$); 1.80 (s, 9H, NHC(C*H*$_3$)$_3$); 1.55 (m, 12H, PC*H*$_2$CH$_3$); 1.40 (s, 9H, NHC(C*H*$_3$)$_3$); 1.25 (br s, 1H, N*H*C(CH$_3$)$_3$); 1.00 (m, 18H, PCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR, C$_6$D$_6$: δ 174.1 (d, J_{P-C} = 14 Hz, *C*O); 52.3, 49.7 (s, NH*C*(CH$_3$)$_3$); 30.5, 26.6 (s, NHC(*C*H$_3$)$_3$); 11.3 (d, J_{P-C} = 34 Hz, P*C*H$_2$CH$_3$); 1.4 (s, PCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR, C$_6$D$_6$: δ 5.9.

Ir(PMe$_3$)$_2$(CO)(H)[C(O)NH(C$_6$H$_4$)], 5. Complex **1** (0.10 g, 0.21 mmol) was dissolved in benzene (15 mL) and the solution was stirred under a CO atmosphere for 12 h. At the end of this period, the volatiles were removed under vacuum and the pale yellow solid residue was extracted with hexane. Cooling the hexane extract at −10 °C for 2 days produced Ir(PMe$_3$)$_2$-(CO)(H)[C(O)NH(C$_6$H$_4$)] as pale yellow microcrystalline solids. The yield was 55%. Found: C, 34.6; H, 5.1; N, 2.3. Calc.: C, 34.1; H, 4.9; N, 2.8. IR, THF, cm^{-1}: 2001 (Ir-CO), 1596 (Ir-C(O)-NH-). ^{1}H NMR, C$_6$D$_6$: δ 8.12 (s, 1H, -C(O)N*H*C$_6$H$_4$); 7.80 (t, J_{H-H} = 6.7 Hz, 1H), 7.10 (t, J_{H-H} = 6.7 Hz, 1H), 6.80 (t, J_{H-H} = 6.7 Hz, 1H), 6.61 (d, J_{H-H} = 7.0 Hz, 1H) (-C(O)NHC$_6$*H*$_4$); 1.45, 0.96 (d, 18H, PC*H*$_3$); −9.25 (dd, J_{P-H} = 118 and 22 Hz, 1H, Ir-*H*). ^{31}P{^{1}H} NMR, C$_6$D$_6$: δ −54.9, −58.6 (d, J_{P-P} = 26 Hz).

Ir(PEt$_3$)$_2$(CO)(H)[C(O)NH(C$_6$H$_4$)], 6. A procedure identical to the one described for the preparation of **5** was adopted. Although by NMR the yield was found to be >90%, the isolated yield was 30%, as separation was difficult due to its high solubility. Found: C, 41.5; H, 6.4; N, 2.4. Calc.: C, 41.6; H, 6.6; N, 2.5. IR, THF, cm^{-1}: 1996 (Ir-CO) and 1599 (Ir-C(O)-NH-). ^{1}H NMR, C$_6$D$_6$: δ 8.20 (s, 1H, -C(O)N*H*C$_6$H$_4$); 7.98 (t, J_{H-H} = 6.4 Hz, 1H), 7.12 (t, J_{H-H} = 6.4 Hz, 1H), 6.85 (t, J_{H-H} = 6.2 Hz, 1H), 6.60 (d, J_{H-H} = 6.7 Hz, 1H) (-C(O)NHC$_6$*H*$_4$); 2.09, 1.58, 1.45, 1.42 (septet, 3H each, PC*H*$_2$CH$_3$); 0.88, 0.70 (5 line multiplet, 9H each, PCH$_2$C*H*$_3$); −9.81 (d of d, 1H, J_{P-H} = 112, 17.5 Hz, Ir-*H*). ^{31}P{^{1}H} NMR, C$_6$D$_6$: δ −15.8, −28.5 (d, J_{P-P} = 18 Hz).

Ir(PEt$_3$)$_2$(CO)$_2$[C(O)NHBu^t], 7. The complex was generated by bubbling CO gas through a solution of **3** (19 mM) in benzene (5 mL). An immediate decoloration of the solution was observed, indicating the formation of **7**. Attempts to isolate the pure complex resulted in an oily substance, which did not give satisfactory elemental analysis. IR, d$_6$-benzene, cm^{-1}: 1961 (m), 1907 (s) (Ir-CO); 1602 (m) (Ir-C(O)-). ^{1}H NMR, C$_6$D$_6$, 30 °C: δ 5.69 (br s, 1H, -C(O)N*H*Bu^t); 1.62 (br m, 12H, PC*H*$_2$CH$_3$); 1.45 (s, 9H, -C(O)NH*Bu^t*); 0.93 (m, 18H, PCH$_2$C*H*$_3$). ^{1}H NMR, d$_8$-toluene, −30 °C: δ 5.95 (s, -C(O)N*H*Bu^t); 1.95, 1.44 (q, PC*H*$_2$CH$_3$); 1.65 (s, -C(O)NH*Bu^t*); 1.11, 0.99 (m, PCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR, d$_8$-toluene, −30 °C: −8.9, −17.3 (d, J_{P-P} = 20 Hz). ^{13}C{^{1}H} NMR (of a sample prepared by passing 99% ^{13}C labelled CO), d$_8$-toluene, −30 °C: 184.1 (m, Ir-*C*O); 156.1 (m, Ir-*C*(O)NHBu^t).

Ir(PEt$_3$)$_2$(CO)(NHBu^t)(PhC≡CPh), 8. A large excess (ca. 10 − 12 fold excess) of PhC≡CPh was added to a solution of **3** (9.0 mM) in benzene (10 mL), and the solution was stirred for 8 h. At the end of this period, the volatiles were removed under vacuum and the resulting waxy solid was transferred to a sublimator. Excess diphenylacetylene was removed from the yellow solid by sublimation at 60 °C (10^{-3} torr pressure). The residual yellow solid contained 90% of Ir(PEt$_3$)$_2$(CO)-(NHBu^t)(PhC≡CPh), **8**; however, **4** was also present as a contaminant and could not be removed by sublimation or recrystallization. As a result, satisfactory elemental analysis

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of **8** could not be obtained. IR, hexane, cm^{-1}: 1945 (Ir-CO). ^{1}H NMR, C_6D_6: δ 7.55 (d, $J_{H\text{-}H}$ = 8.0 Hz, 4H), 7.21 (t, $J_{H\text{-}H}$ = 8.0 Hz, 4H), 7.06 (t, $J_{H\text{-}H}$ = 8.0 Hz, 2H) (*Ph*C≡C*Ph*); 5.11 (s, 1H, N*H*Bu^t); 2.09, 1.61 (m, 12H, PCH_2CH_3); 1.23 (s, 9H, -NH*Bu^t*); 0.91 (m, 18H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR, C_6D_6: −1.7. $^{13}C\{^1H\}$ NMR, C_6D_6: δ 142.9 (t, $J_{P\text{-}C}$ = 9 Hz, PhC_2Ph).

Ir(PEt$_3$)$_2$(CO)(H)(C≡CPh)$_2$, 9. To a solution of **3** (0.10 g, 0.19 mmol) in benzene was added PhC≡CH (42 μL, 0.38 mmol) dropwise. During the addition, the initial bright yellow color of the solution gradually turned pale yellow. Once the addition was complete, the reaction mixture was allowed to stir for 0.5 h, after which time the volatiles were removed under vacuum and the residual solid was dissolved in hexane. Concentrating the hexane solution and cooling it to −10 °C for 2 days yielded $Ir(PEt_3)_2(CO)(H)(C{\equiv}CPh)_2$ as a pale yellow microcrystalline solid. The yield was 44%. IR, THF, cm^{-1}: 2118, 2027, 1996. ^{1}H NMR, C_6D_6: δ 7.45 (d, $J_{H\text{-}H}$ = 8.3 Hz, 4H), 7.10 (t, $J_{H\text{-}H}$ = 8.3 Hz, 4H), 6.99 (t, $J_{H\text{-}H}$ = 8.3 Hz, 2H) (-C≡C*Ph*); 1.90 (m, 12H, PCH_2CH_3), 1.00 (m, 18H, PCH_2CH_3); −9.70 (t, $J_{P\text{-}H}$ = 19.2 Hz, 1H, Ir-*H*). $^{13}C\{^1H\}$ NMR, C_6D_6: δ 172.6 (Ir-*C*O); 106.5 (s, Ir-C≡*C*Ph); 77.0 (t, $J_{P\text{-}C}$ = 12.5 Hz, Ir-*C*≡CPh), 18.9 (t, $J_{P\text{-}C}$ = 75 Hz, PCH_2CH_3), 8.0 (s, PCH_2CH_3). $^{31}P\{^1H\}$ NMR, C_6D_6: δ −8.5.

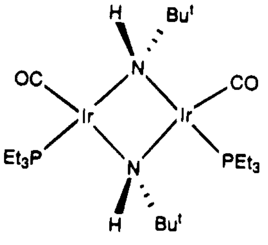
Results and Discussion

Synthesis of *trans*-Ir(PR$_3$)$_2$(CO)(NHPh) (PR$_3$ = PMe$_3$ (1), PEt$_3$ (2)). The anilide complexes *trans*-Ir(PR$_3$)$_2$(CO)(NHPh), **1** (PMe$_3$) and **2** (PEt$_3$), were formed in high yields in reactions between *trans*-Ir(PR$_3$)$_2$(CO)Cl and LiNHPh in THF. Similar to the synthesis of the analogous PPh$_3$ complexes, a three-fold excess of the lithium salt was used in the reaction. The products were separated from excess LiNHPh and LiCl by extraction of the crude mixture with hexane. Final purification was carried out by sublimation. Both complexes show extreme sensitivity to oxygen and moisture in solution and solid states.

Characterization of **1** and **2** was carried out by elemental analyses and spectroscopic methods. Complex **1** displays an IR band for the CO ligand at 1935 cm^{-1}, ca. 10 cm^{-1} lower than that in the PPh$_3$ analog. This lowering parallels the higher basicity of PMe$_3$ over PPh$_3$. The CO stretching frequency for complex **2** was observed at 1931 cm^{-1}, again consistent with a slightly higher basicity of PEt$_3$ over PMe$_3$. Due to the mutual trans orientation of the phosphines, the ^{31}P NMR spectra of **1** and **2** show a single resonance. The effect of virtual coupling causes the P*Me*$_3$ resonance to appear as a pseudo-triplet in the ^{1}H NMR spectrum. The same effect is responsible for a complex multiplicity pattern of the P*CH*$_2$CH$_3$ resonance in **2**. The phenyl hydrogens give rise to three signals – a doublet for the ortho protons and a triplet for each of the meta and para protons. A somewhat broad singlet with no resolved phosphorus coupling is identifiable for the -N*H*- protons.

Synthesis of *trans*-Ir(PEt$_3$)$_2$(CO)(NHBu^t), 3. A very clean reaction occurs between *trans*-Ir(PEt$_3$)$_2$(CO)Cl and LiNH^{t}Bu in benzene to give complex **3** nearly quantitatively (by NMR). Attempts to isolate the complex, however, resulted in a mixture containing **3** and the dimeric complex [Ir(PEt$_3$)(CO)(μ-NHBu^t)]$_2$ (*vide infra*). The quantitative formation of **3** was a surprise in light of our earlier failures in synthesizing such a complex with PPh$_3$ or PMe$_3$ as coligands. The characterization of **3** was made possible by ^{1}H NMR and IR spectroscopy. An NMR spectrum was recorded after a 1:1 mixture of *trans*-Ir(PEt$_3$)$_2$(CO)Cl and LiNHBu^t was allowed to react in C_6D_6 for 3 h and the LiCl precipitate was removed by filtration. An inspection of the spectrum reveals that the resonances for the PEt$_3$ ligand remain virtually unchanged in terms of their chemical shift positions and multiplicity pattern in going from the chloro complex to the amido complex. Similarly, the Bu^t resonance does not show any significant chemical shift change either. The -N*H*- resonance, however, undergoes a marked shift: it moves from δ −0.50 in LiNHBu^t to δ 1.68 in the metal complex. Analogous to its arylamide counterpart, complex **3** displays a single resonance in the ^{31}P NMR spectrum. The CO band is observed at 1905 cm^{-1}, a value which is 26 cm^{-1} lower than that for **2**, thus indicating a more basic metal center in **3**.

Dimerization of *trans*-Ir(PEt$_3$)$_2$(CO)(NHBu^t). Benzene solutions of *trans*-Ir(PEt$_3$)$_2$(CO)(NHBu^t), **3**, when subjected to heat or vacuum, readily convert to a dimeric species, [Ir(μ-NHBu^t)(CO)(PEt$_3$)]$_2$, **4**, which can be isolated and characterized by elemental analysis and spectroscopic methods. Free PEt$_3$ can be detected when the reaction is monitored by ^{31}P NMR spectroscopy. Analogous to its monomeric precursor, complex **4** exhibits high solubility in almost all commonly used solvents and could only be isolated at −78 °C from pentane. The proposed structure is justified as follows: (1) one phosphine resonance is observed in the ^{31}P NMR spectrum; (2) the presence of two CO bands in the IR spectrum suggests a mutually cis arrangement of the CO ligands; (3) two different ^{1}H resonances for both the Bu^t and the -NH- protons indicate that the -NHBu^t ligands are inequivalent; (4) the triplet nature of the -N*H*- resonance at δ 3.25 shows this proton to be coupled to both phosphines, thus suggesting a bridging coordination mode for at least one of the NHBu^t groups; and (5) only one ^{13}C resonance (doublet) is observed for the CO ligands. In addition to the NMR evidence, the mass spectrum of **4** shows molecular ion peaks at 821 and 823 m/e (^{191}Ir and ^{193}Ir), further confirming the dimeric nature of the complex. In order to ascertain the relative orientation of the two Bu^t groups, an NOE experiment was carried out. It was observed that irradiation of one Bu^t resonance caused enhancement (ca. 7.5%) in the intensity of the other Bu^t resonance, suggesting their cis orientation.



4

Reactions of 1 and 2 with CO. The carbonylation reactions of *trans*-Ir(PPh$_3$)$_2$(CO)(NHAr), where Ar = Ph, *o*-tolyl, *p*-tolyl, *p*-C_6H_4Cl, 2,6-$C_6H_3Me_2$ and 3,5-$C_6H_3Me_2$, show that rapid insertion of CO into the Ir-amide bond occurs and that the resulting carbamoyl moiety undergoes orthometallation when ortho sites are available on the Ar group.[7(b)] We find that complexes **1** and **2** exhibit identical behavior. Passage of CO through a benzene solution of either **1** or **2** results in orthometallated products having the same structure as shown for **III**.

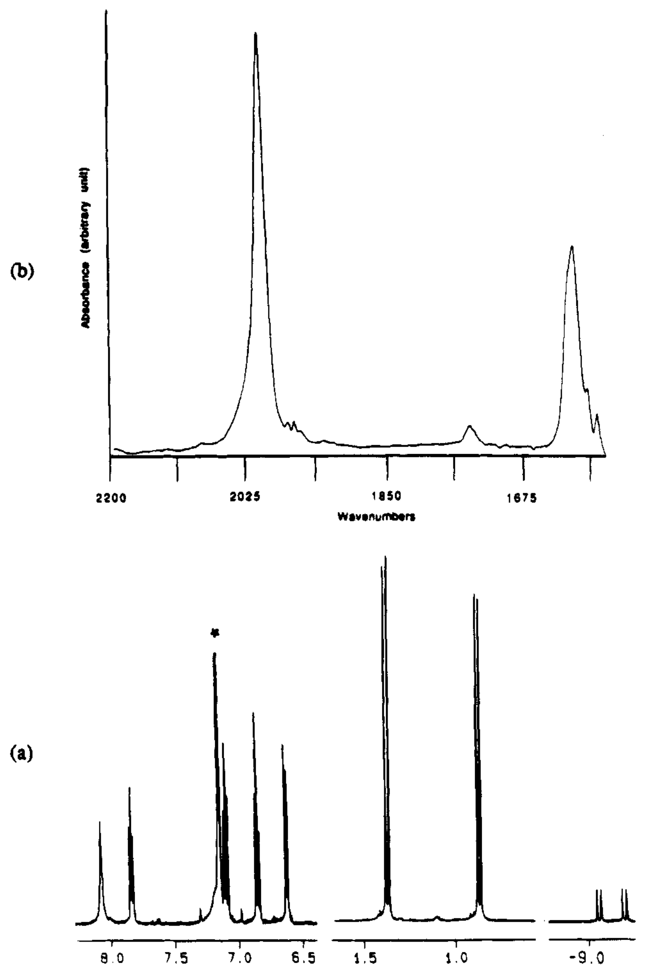
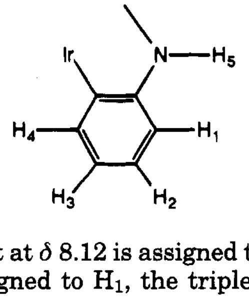


Figure 1. 500 MHz ^{1}H NMR (a) and IR (b) spectra of Ir(PMe$_3$)$_2$(CO)(H)[C(O)NH(C$_6$H$_4$)], **5**. The resonance marked with an asterisk is due to protio impurity of C$_6$D$_6$.

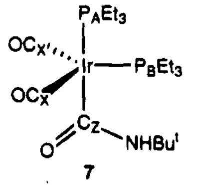
The ^{1}H NMR spectral characterization of **III** involved a certain degree of ambiguity due to the overlap of aromatic resonances. Additionally, the -NH- resonance of the orthometallated ring was not clearly visible. The ^{1}H NMR (500 MHz) spectra of **5** and **6** provide an unambiguous spectral analysis of these complexes by being able to account for every single proton in these molecules. As can be seen in the spectrum of **5** (Figure 1(a)), the aromatic region shows five resonances. A ^{1}H COSY NMR experiment provided unambiguous assignment of these resonances, which are as follows(use the proton numbering scheme shown in the following diagram):



The broad singlet at δ 8.12 is assigned to H$_5$, the doublet at δ 6.61 is assigned to H$_1$, the triplets at δ 6.80 and 7.10 are assigned to H$_2$ and H$_3$, respectively, and the triplet at δ 7.80 is assigned to H$_4$. The triplet nature of H$_4$ arises due to coupling to both H$_3$ and the phosphorus trans to the aryl ligand. Inequivalent PMe$_3$ ligands give rise to two doublets at δ 0.91 and 1.40. The hydride resonance at δ −9.25 shows a doublet of doublets splitting pattern, with $J_{P\text{-}H}$ of 118 and 22 Hz. The larger coupling is due to the trans phosphine and the smaller one is due to the cis. An identical splitting pattern is observed for complex **6**.

Reaction of 3 with CO. Bubbling CO gas through a benzene solution of **3** results in its rapid decolorization and the formation of the CO-inserted product Ir(PEt$_3$)$_2$(CO)$_2$[C(O)NHBu^t], **7**, which has been characterized by a multinuclear NMR study. The room temperature ^{1}H NMR (500 MHz) spectra of a reaction mixture in d$_6$-benzene before and after the passage of CO show the following changes: the PCH_2CH$_3$ multiplets at δ 1.83 move to δ 1.65 and become broad; the PCH$_2$CH_3 multiplet, though moves to higher field, remains sharp; the -NH- resonance at δ 1.68 disappears and a new broad one grows at δ 5.70. This large downfield shift is indicative of the formation of the -C(O)NH- moiety. The singlet due to the Bu^t group remains unshifted.

At room temperature, the ^{31}P{^{1}H} NMR (202.5 MHz) spectrum displays an extremely broad resonance which is barely visible above the baseline. Upon cooling the sample to −28 °C, the broad signal splits into two well-resolved doublets (δ −8.9 and −17.2, $J_{P\text{-}P}$ = 18 Hz), as shown in Figure 2(b). Concomitant with decoalescence of the phosphorus resonances, the methyl and methylene ^{1}H NMR resonances of the PEt$_3$ ligands each split into two (Figure 2(a)). The IR spectrum shows *two* bands for terminal COs, as well as a low frequency band for the carbamoyl ligand. In order to ascertain the relative orientation of the ligands in **7**, a reaction between **3** and 99% ^{13}C labelled CO was carried out in an NMR tube, and the reaction mixture was analyzed by ^{31}P and ^{13}C NMR spectroscopy. The spectral features, as described below, are consistent with the following structure for **7**, where the ligating atoms are labelled in accordance with the spin system that they generate:



7

The ^{13}C{^{1}H} NMR (125.8 MHz) spectrum of ^{13}C-enriched **7** displays two low-field resonances at −28 °C – the resonance at δ 184.2, which is a multiplet with four lines of equal intensity, is assigned to the terminal CO ligands, and the resonance at δ 156.1, which is a doublet of multiplets, is assigned to the -C(O)- of the carbamoyl ligand. The four-line, or a doublet of doublets, pattern of the resonace due to the C$_X$ atoms arises from different coupling to two non-equivalent phosphorus atoms. The equatorial P$_B$ atom shows a larger coupling, $J_{P\text{-}C}$ = 24 Hz, while the smaller coupling, $J_{P\text{-}C}$ = 12 Hz, is due to the axial P$_A$. It appears that coupling between C$_X$ and C$_Z$ atoms is not resolved. Naturally, the largest coupling is observed for the trans ligands, P$_A$ and C$_Z$, with a $J_{P\text{-}C}$ of 78 Hz.

The ^{31}P{^{1}H} NMR (202.5 MHz) spectrum of this ^{13}C-labelled sample shows a more complex pattern (Figure 2(c)). The multiplet centered at δ −8.9 is assigned to P$_B$, the equatorial phosphine ligand. Qualitatively, the overall quartet-like shape of this multiplet can be

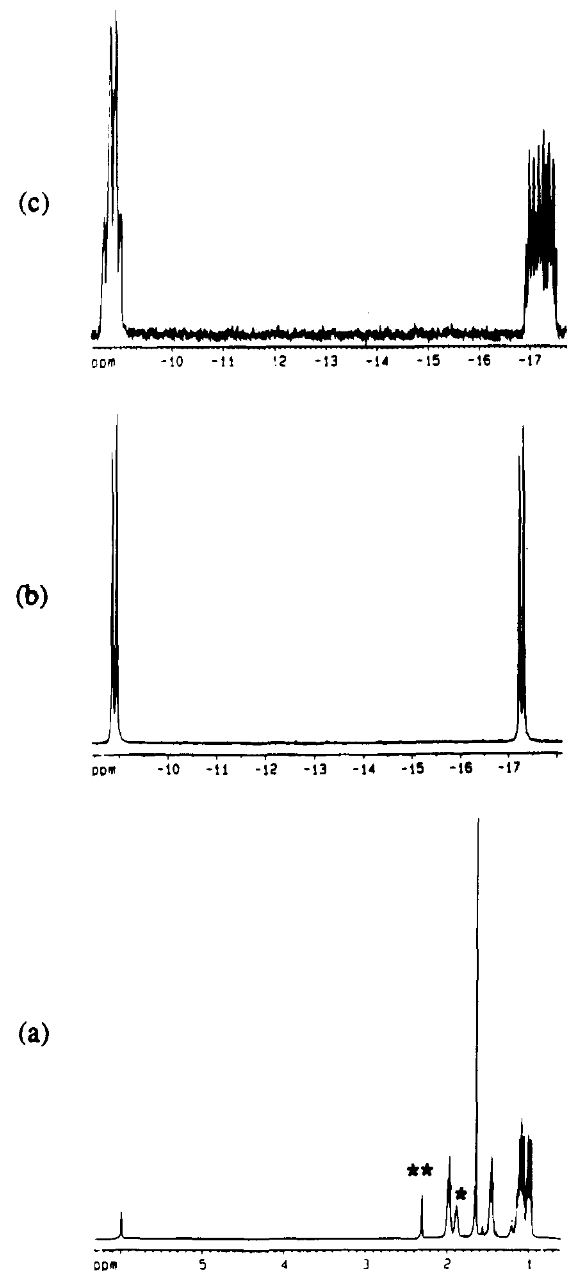


Figure 2. (a) ^{1}H NMR (500 MHz) spectrum at −28 °C of a reaction mixture containing **3** and CO to generate Ir$(PEt_3)_2(CO)_2[C(O)NHBu^t]$, **7**, as the major product. Asterisk denotes an unknown impurity and double asterisk denotes protio impurity of d_8-toluene. (b) $^{31}P\{^1H\}$ NMR (202.5 MHz) spectrum of the same reaction mixture at −28 °C. (c) $^{31}P\{^1H\}$ NMR spectrum at −28 °C when 99% ^{13}C-labelled CO gas was used in the reaction.

rationalized in terms of an overlapping triplet of doublets [$J(P_B\text{-}C_X)$ = 24 Hz, $J(P_A\text{-}P_B)$ = 18 Hz], with additional splitting due to coupling between P_B and C_Z ($J(P_B\text{-}C_Z)$ = 8 Hz). However, the resonance is more complex than predicted by this set of coupling constants. Similarly, the resonance for P_A at δ −17.2 shows a multiplicity more complex than that arising from coupling between P_A-C_Z (J = 78 Hz), P_A-P_B and P_A-C_X (J = 12 Hz). The additional multiplicity for both resonances can be explained by considering the sample to be a mixture of 40% **7** that lacks ^{13}C labelling at the carbamoyl-carbon atom and 60% **7** that is fully labelled. For the minor component, the large trans coupling between P_A and C_Z and the small cis coupling between P_B and C_Z will be absent, thereby increasing the complexity of the two phosphine resonances from superposition of the spectra due to the two species. Using complete line-shape simulation methods,[9] the multiplicity of the ^{31}P resonances of the ^{13}C-carbamoyl and ^{12}C-carbamoyl containing species have been determined and are shown in Figures 3(a) and 3(b), respectively. Figure 3(c) represents a composite spectrum, incorporating 60% ^{13}C-carbamoyl and 40% ^{12}C-carbamoyl containing species. As can be seen, the fit of the theoretical spectrum to the experimental one (Figure 3(d)) is nearly perfect.

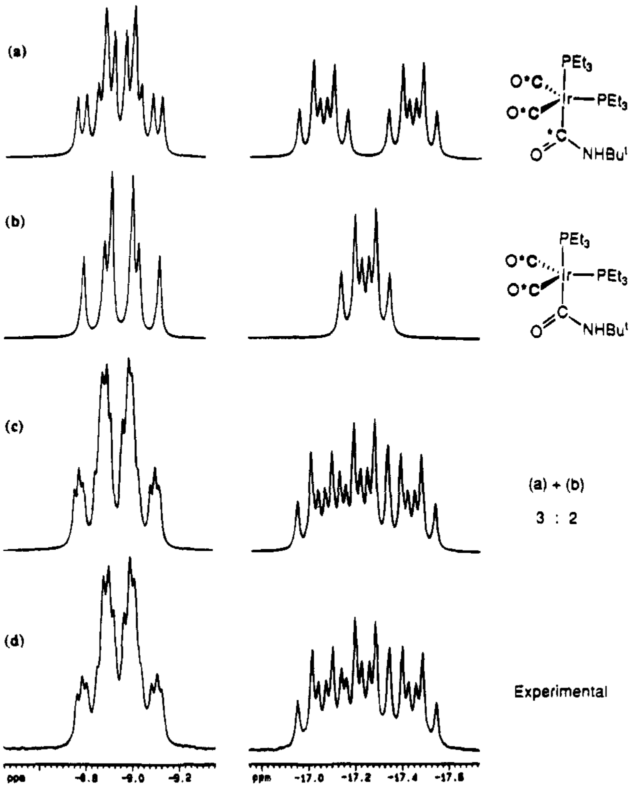


Figure 3. (a) Theoretical ^{31}P NMR spectrum of $Ir(PEt_3)_2(^*CO)_2[^*C(O)NHBu^t]$, where *C denotes ^{13}C. See text for the various coupling constants. (b) Theoretical ^{31}P NMR spectrum of $Ir(PEt_3)_2(^*CO)_2[C(O)NHBu^t]$. (c) A composite spectrum of 60% $Ir(PEt_3)_2(^*CO)_2[^*C(O)NHBu^t]$ and 40% $Ir(PEt_3)_2(^*CO)_2[C(O)NHBu^t]$. (d) Expanded regions of the experimental spectrum shown in Figure 2(c).

The reactivity of **3** towards CO is analogous to that we observed for *trans*-$Ir(PPh_3)_2(CO)[NH(2,6\text{-}Me_2C_6H_3)]$,[7(b)] which produces the dicarbonyl-carbamoyl complex $Ir(PPh_3)_2(CO)_2[C(O)NH(2,6\text{-}Me_2C_6H_3)]$. Structurally, however, this complex is quite different from **7**, having all of the bulky ligands in the equatorial sites, as one would expect on steric ground. Although CO in an axial position cannot be as effective a back-bonder as in an equatorial site, the presence of PPh_3 probably makes up for this deficiency. Since there are no other π-acid ligands in **7** except for CO, one can argue that the need to maximize Ir-CO back-bonding becomes the determining factor in producing the observed structure. It must be noted that fluxionality in **7** is observed at room temperature, and it is quite possible that a different structure is adopted at higher temperatures. Due to its rapid decomposition, we were not able to carry out any structural analysis at higher temperatures.

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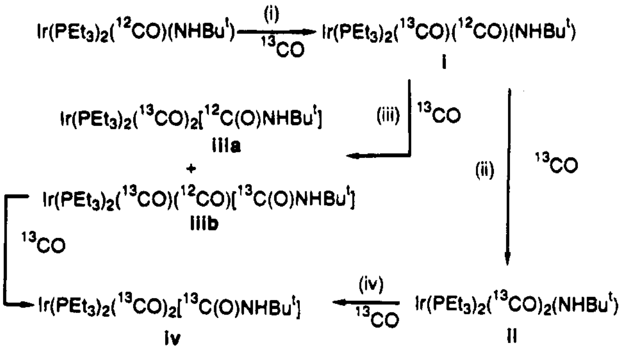
[9] Spectral simulations were performed by using a locally modified version of UEANMR: Harris, R. K.; Woodman, C. M. Program no. 188, QCPE, Indiana University, Bloomington; *Mol. Phys.* **1966**, *10*, 437.

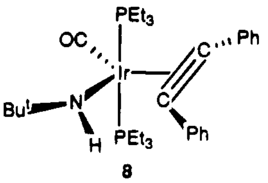
Scheme 1



A probable reason for the incorporation of ^{12}CO in forming the carbamoyl ligand is described in Scheme 1. Since the starting complex **4** possesses ^{12}CO, the dicarbonyl complex, **i**, formed in step (i), will initially contain both ^{12}CO and ^{13}CO. Step (ii) represents the process of ^{12}CO exchanging with ^{13}CO to give fully labelled dicarbonyl **ii**. Insertion of the NHBu^t ligand in **i** (step (iii)) will generate both ^{12}C(O)- and ^{13}C(O)-containing carbamoyl species **iiia** and **iiib**, respectively. On the other hand, insertion in **ii** will produce only ^{13}C(O)-containing species **iv**. The presence of excess ^{13}CO will convert **iiib** to **iv**, thus generating a final mixture of only two species, **iiia** and **iv**, in solution. The relative amounts of these two species depend on the rate of ^{13}CO purge during the reaction, clearly showing that step (ii) is in competition with step (iii).

We should point out, however, that the intermediacy of a dicarbonyl species has never been directly observed, only inferred. Due to its extreme solubility and oil-like texture, complex **7** could not be isolated in pure form for elemental analysis.

Reaction of 3 with PhC≡CPh. When a five- to tenfold excess of diphenylacetylene is reacted with **3** in benzene for ca. 8 h, the formation of Ir(PEt$_3$)$_2$(CO)(NHBu^t)(PhC≡CPh), **8**, can be evidenced by ^{1}H NMR spectroscopy. In C$_6$D$_6$, the aromatic protons of the coordinated alkyne display three resonances – a doublet and two triplets – indicating equivalent phenyl groups. Likewise, a total of four aromatic resonances are observed in the ^{13}C{^{1}H} NMR spectrum. The PhC$_2$Ph resonance appears at δ 142.9 as a triplet ($J_{\text{P-C}}$ = 6.5 Hz), which is consistent with the ligand being a two electron donor.[10] A single resonance is observed in the ^{31}P{^{1}H} NMR spectrum. These features, along with the diastereotopic nature of the PCH_2CH_3 resonances, are consistent with the following structure for complex **8**:

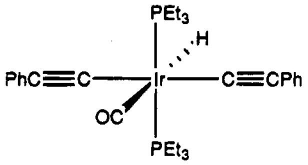


8

The two phenyl rings are made equivalent by rapid rotation of the alkyne ligand on the NMR time scale. Although PhC≡CPh is considered to be a π-acid, the presence of which can cause the -NH- resonance to shift downfield due to its increased acidity, the observed shift of more than 3 ppm is too large for this to be the only factor. Generally, such large shifts are associated with insertion of CO into the metal-amide bond, which is ruled out in this case by IR spectroscopy. It is possible that the large shift is in part due to the magnetic anisotropy of the carbon-carbon triple bond.

The formation of **8** always accompanies a small amount of the dimer, **4**. Due to the high solubility of both these complexes, analytically pure samples of **8** could not be obtained.

Reaction of 3 with PhC≡CH. The reaction of two or more equivalents of PhC≡CH with *trans*-Ir(PEt$_3$)$_2$(CO)(NHBu^t) produces the hydrido bis-alkynyl complex Ir(PEt$_3$)$_2$(CO)(H)(C≡CPh)$_2$, **9**, which can be isolated as a yellow microcrystalline solid from hexane. Although we have not been able to obtain X-ray quality crystals yet, elemental and spectroscopic analyses are consistent with the above formulation. The ^{1}H NMR spectrum reveals equivalent alkynyl and phosphine ligands. The triplet resonance at δ −9.75 is assigned to the hydride ligand; the multiplicity pattern and the observed $J_{\text{P-H}}$ of 12 Hz clearly show that the hydride is cis to the phosphines. In the ^{13}C{^{1}H} NMR spectrum, four aromatic resonances are observed for the σ-alkynyl ligand. As expected, the alkynyl carbon atoms give rise to two separate ^{13}C resonances, one of which is a triplet (δ 77.1, $J_{\text{P-C}}$ = 12.5 Hz) and the other a singlet (δ 106.2). The triplet nature of the higher field resonance prompts us to assign it to the carbon atom σ-bonded to the metal. The observed small $J_{\text{P-C}}$ is a clear indication of the cis orientation of the alkynyl ligands with respect to the phosphines. These observations are consistent with the structure



9

Transition metal complexes containing both σ-alkynyl and carbonyl ligands give rise to strong absorption bands in the range 2200 − 1900 cm^{-1} arising from both these ligands,[11] thus making unambiguous assignment rather difficult. When two alkynyl ligands are present, coupling of ν(C≡C) vibrations of the two ligands sometimes result in split bands.[12] The situation becomes even more complicated when a hydride ligand is present along with CO and σ-alkynyl groups – coupling of M-H, M-C≡O and M-C≡CR vibrations ensue. For complex **9**, five bands are visible in the range 2200 − 1900 cm^{-1} in the IR spectrum: 2118 (vs), 2102 (sh, m), 2027 (w), 1996 (s) and 1946 (w). It is not possible at this stage to make correct band assignment without isotopic labelling.

The formation of **9** is preceded by the monoalkynyl complex *trans*-Ir(PEt$_3$)$_2$(CO)(C≡CPh), which can be detected by IR and NMR spectroscopy when one equiv of PhC≡CH is added to **3**.[13] It is not clear whether the

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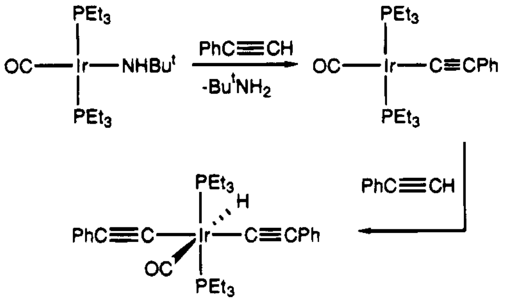
(10) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(11) (a) Bennett, M. A.; Charles, R.; Fraser, P. J. *Aust. J. Chem.* **1977**, *30*, 1213. (b) Walter, R. H.; Johnson, B. F. G. *J. Chem. Soc. Dalton Trans.* **1978**, 381.

(12) (a) Furlani, A.; Licoccia, S. Russo, M. V. *J. Chem. Soc. Dalton Trans.* **1984**, 2197. (b) Furlani, A.; Russo, M. V. *J. Organomet. Chem.* **1979**, *165*, 101.

monoalkynyl complex is formed by oxidative addition of PhC≡CH to **3** followed by reductive elimination of Bu^tNH_2, or by direct protonation of the amide ligand by PhC≡CH. In any case, complex **9** is clearly an oxidative addition product of PhC≡CH and *trans*-Ir$(PEt_3)_2$(CO)(-C≡CPh). The overall reaction sequence is



As the above reaction sequence shows, the two alkynyl moieties are added in a stepwise fashion, which is a desirable feature if one wishes to incorporate trans alkynyl ligands with different end groups. Chow *et al* reported such a synthetic scheme to prepare *mer-trans*-Rh$(PMe_3)_3$(H)(C≡CPh)$_2$ from Rh$(PMe_3)_4$(Me) by stepwise addition of PhC≡CH.[14] We are currently examining the reactivity of HC≡CH with **3** and related complexes.

Acknowledgment. We wish to thank Johnson Matthey/Alfa/Aesar for a generous loan of iridium chloride, Mr. Jim Breeyear and Mr. Robert Hayes for their help with NMR experiments, and Mr. Bob Bennett for obtaining the mass spectrum of **4**. The 500–MHz NMR instrument was purchased through a grant from NSF (CHE-9208434).

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(13) Spectral data for *trans*-Ir$(PEt_3)_2$(CO)(-C≡CPh): IR, hexane, cm^{-1}: 1944. ^1H NMR, C_6D_6: δ 7.49 (d, 2H), 7.10 (t, 2H), 6.95 (t, 1H) (-C≡C*Ph*); 1.90 (m, 12H, PCH_2CH_3); 1.05 (m, 18H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR, C_6D_6: δ 16.0.

(14) Chow, P.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc. Chem. Comm.* **1989**, 1545.