Preparation of alkynepentacarbonyltriphenylphosphinedicobalt complexes using ultra violet light

James C. Anderson *, Brian F. Taylor, Clare Viney, Graham J. Wilson

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

Received 1 November 1995

Abstract

The preparation of alkynepentacarbonyltriphenylphosphinedicobalt complexes under mild conditions using linearly polarised ultra violet laser light is described. This method compares favourably with conventional thermal techniques and is superior when the alkyne contains reactive functional groups.

Keywords: Carbonyl; Cobalt; Alkyne; Phosphine; Photochemistry

1. Introduction

During our studies on the effect of circularly polarised laser light on alkyne dicobalt complexes 1 (L = CO) in the presence of triphenylphosphine [1] we needed to prepare alkynepentacarbonyltriphenylphosphinedicobalt complexes 2 (L = PPh$_3$) for characterisation purposes. For control studies these complexes were prepared using photolytically induced substitution of a carbonyl for a triphenylphosphine ligand. A variety of complexes where L is a simple phosphine is known [2,3] and these types of complex where the phosphine contains a chiral substituent are important in efficient enantioselective variants [4] of the Pauson–Khand reaction [5]. The replacement of a CO by a phosphine has been carried out using elevated temperatures [6] over prolonged reaction times [2,3]. Using these thermal techniques it is sometimes difficult to control the reaction to produce only monosubstituted complexes without contamination by products of higher substitution [7]. Some milder electrochemical or electron-transfer catalysed methods have been investigated but substrate generality is limited [8]. The use of photolytic techniques, despite the great facility with which metal carbonyl bonds are cleaved with strong light [9], is limited to a single disubstitution reaction [10].

We wish to report our studies comparing the preparation of complexes 2 photolytically against conventional thermal techniques. The results presented here complement the studies of Kerr et al. presented in a preceding paper [11], which reveals consistently high yielding preparations of phosphorus containing alkyne–dicobalt complexes using trimethylamine N-oxide.dihydrate.

2. Results and discussion

We prepared a variety of alkynehexacarbonyldicobalt complexes 1 (Fig. 1) by the standard method [12]. These were then transformed into their pentacarbonyltriphenylphosphine complexes 2 by heating to 60–70°C in toluene (0.15–0.6 M) in the presence of one equivalent of triphenylphosphine for 4 h and by irradiating toluene solutions (0.01–0.03 M) for 7 h at room temperature, also in the presence of one equivalent of triphenylphosphine with linearly polarised ultra violet laser light (Table 1).

The photolytic method described is very gentle, yields are moderate to excellent and compare favourably with the traditional thermal technique. In particular, it should
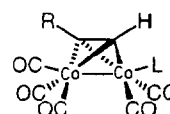
1 L=CO   2 L=PPh$_3$

a, R=Ph; b, R=*n*Bu; c, R=CH$_3$OCH$_2$; d, R=CH$_3$OCO.; e, R=Ac

Fig. 1.

* Corresponding author.

Table 1
Preparation of complexes 2

Complex	Thermal yield (%)	Photolytic yield (%)
a	88	86
b	81	50
c	85	50
d	64	84
e	60	96

be noted that functionalised and potentially sensitive alkynes (2d and 2e) gave excellent yields photolytically over the thermal conditions. Furthermore, the formation of polysubstituted phosphine products was not detected in any of the photolytic experiments. We currently have no explanation for the moderate yields of compounds 2b and 2c in comparison with the thermal technique.

These types of compound (2), we found, were poorly characterised in the literature and we undertook extensive spectroscopic characterisation to verify the formation of these complexes. The most striking spectroscopic characteristics of complexes 2 are in the ^{1}H NMR spectrum where the terminal alkyne proton appears at a low field shift as a distinctive doublet due to $^3J_{PH}$ coupling in the range around 3–5 Hz (Table 2). Another distinctive characteristic can be found in the ^{13}C NMR spectrum where the CO ligands are chemically distinct and often appear in the ratio 3 : 1 : 1 with respect to intensity [13] (Table 2). This corresponds to Co(CO)$_3$ and the pseudo axial/equatorial CO ligands at the other cobalt metal centre. All other spectroscopic data were in full agreement with the assigned structures.

In conclusion this study has shown that alkynepentacarbonyltriphenylphosphinedicobalt complexes 2 can be prepared under remarkably mild conditions, using linearly polarised ultra violet laser light, from the parent hexacarbonyl complex 1 in fair to excellent yields. This procedure may find application for the preparation of these and related complexes [4,11] where the alkyne substituent contains sensitive functionality.

3. Experimental

3.1. General

All reagents were obtained from commercial suppliers and used without further purification. Solvents were

Table 2
Selected NMR data for complexes 2

Complex	$\delta(\equiv CH)(^3J_{PH})$	$\delta(CO)$ (intensity)
a	5.37(4.5)	201.5(3), 204.6(1), 205.8(1)
b	5.13(3.9)	202.3(3), 205.1(1), 206.2(1)
c	5.08(3.0)	201.7(3), 204.9(1), 205.6(1)
d	5.23(4.7)	200.2(3), 204.4(2)
e	5.24(4.9)	200.3(3), 204.4(2)

purified by standard procedures as necessary. Analytical thin layer chromatography was performed using Merck 5554 60F silica gel coated aluminium plates, visualisation was effected using ultra violet light or by development using ceric ammonium molybdate. Flash column chromatography was performed on aluminium oxide neutral (50–160 μM). Petrol refers to petroleum ether, b.p. 40–60°C, which was distilled prior to use. ^{1}H and ^{13}C NMR were recorded in CDCl$_3$ on a Bruker AC-250 NMR spectrometer supported by an Aspect 3000 data system and an automated sample changer, and on an AMX2 400 NMR, using residual protic solvent CHCl$_3$ (δ_H = 7.25 ppm) or CDCl$_3$ (δ_C = 77.0 ppm, t) as internal reference. ^{31}P NMR were recorded with respect to 85% ortho-phosphoric acid. Coupling constants are measured in hertz. Infra red spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer as a thin film. Mass spectra were recorded using a Krakos MS80 spectrometer. Linearly polarised light was produced from a Coherent Innova 304 Ar-ion continuous wave through a linear polariser PHU 10 (from optics for research) that consists of two air spaced calcite prisms. The irradiations (351.1, 351.4 and 363.8 nm, jointly, ca. 0.28 mW) were carried out in a well-stirred reactor made from a round bottomed flask with a built on cell of 20 cm total optical path and 2 cm internal diameter provided with Suprasil optical windows.

3.2. General procedure for the thermal preparation of alkynepentacarbonyltriphenylphosphinedicobalt complexes 2

A solution of alkynehexacarbonyldicobalt complex 1 and triphenylphosphine (1 equiv.) in anhydrous toluene (0.15–0.6 M) was heated at 60–70°C under nitrogen. After approximately 4 h the reaction mixture was cooled, evaporated to dryness in vacuo and the resultant red oil was purified by flash column chromatography.

3.3. General procedure for the photolytic preparation of alkynepentacarbonyltriphenylphosphinedicobalt complexes 2

A solution of alkynehexacarbonyldicobalt complex 1 and triphenylphosphine (1 equiv.) in anhydrous toluene (0.01–0.03 M) was irradiated, under nitrogen, with linearly polarised laser light at wavelengths 351.1, 351.4 and 363.8 nm. After 7 h the reaction mixture was evaporated to dryness in vacuo and the resultant red oil was purified by flash column chromatography.

3.4. Phenylacetylenepentacarbonyltriphenylphosphinedicobalt complexes 2a

Thermally: 1a (147 mg, 0.38 mmol), PPh$_3$ (100 mg, 1 equiv.) in toluene (10 ml) gave 2a (208 mg, 88%).

Photolytically: **1a** (105 mg, 0.28 mmol), PPh_3 (71 mg, 1 equiv.) in toluene (100 ml) gave **2a** (111 mg, 84%).

R_f 0.38, 2% ether–petrol. ^1H NMR: δ 5.37 (1H, d, $J = 4.5$, $\equiv CH$); 7.35–7.55 (20H, m, Ar, PPh_3). ^{13}C NMR: δ 71.2 ($\equiv CH$); 86.0 ($\equiv CPh$); 128.2–133.0 (m, Ar); 201.5 (3CO); 204.6 (CO); 205.8 (CO). ^{31}P NMR: δ 52.8 (P–Co). IR: ν_{max} (film) 3057.8, 2060.5, 2008.8, 1961.9 cm^{-1}. MS: m/z 622 (M^+), 594 (M^+–CO), 566 (M^+–2CO), 538 (M^+–3CO), 510 (M^+–4CO), 482 (M^+–5CO). Anal. Found (MH$^+$): 622.9859. $C_{31}H_{22}Co_2O_5P$ Calc.: 622.9869.

3.5. 1-Hexynepentacarbonyltriphenylphosphinedicobalt complexes 2b

Thermally: **1b** (100 mg, 0.27 mmol), PPh_3 (72 mg, 1 equiv.) in toluene (10 ml) gave **2b** (153 mg, 81%).

Photolytically: **1b** (100 mg, 0.27 mmol), PPh_3 (72 mg, 1 equiv.) in toluene (100 ml) gave **2b** (82 mg, 50%).

R_f 0.4, 5% ether–petrol. ^1H NMR: δ 0.71 (3H, t, $J = 7.2$, CH_3); 1.52 (4H, dq, m, $2 \times CH_2$); 1.53 (2H, t, m, CH_2); 5.13 (1H, d, $J = 3.9$, $\equiv CH$); 7.16–7.45 (15H, m, Ar, PPh_3). ^{13}C NMR: δ 3.8 (CH_3CH_2); 22.3 (CH_3CH_2); 32.3 ($CH_3CH_2CH_2$); 33.8 ($CH_3CH_2CH_2$-CH_2); 72.2 ($\equiv CH$); 94.5 ($\equiv CC_4H_9$); 128.4–137.2 (m, Ar, PPh_3); 202.3 (3CO); 205.1 (CO); 206.2 (CO). IR: ν_{max} (film) 2925.1, 2060, 2007.9 cm^{-1}. MS: m/z 602 (M^+), 574 (M^+–CO), 546 (M^+–2CO), 518 (M^+–3CO), 590 (M^+–4CO), 462 (M^+–5CO). Anal. Found (M^+): 602.0093. $C_{29}H_{25}Co_2O_5P$ Calc.: 602.0104.

3.6. Methylpropargyletherpentacarbonyltriphenylphosphinedicobalt complexes 2c

Thermally: **1c** (49 mg, 0.14 mmol), PPh_3 (36 mg, 1 equiv.) in toluene (10 ml) gave **2c** (70 mg, 85%).

Photolytically: **1c** (49 mg, 0.14 mmol), PPh_3 (38 mg, 1 equiv.) in toluene (100 ml) gave **2c** (55 mg, 50%).

R_f 0.4, 10% ether–petrol. ^1H NMR: δ 3.13 (3H, s, CH_3); 3.73 (1H, d, $J = 12.5$, CH_3OCH_2); 3.96 (1H, d, $J = 13.1$, CH_3OCH_2); 5.08 (1H, d, $J = 3.0$, $\equiv CH$); 7.18–7.45 (15H, m, Ar, PPh_3). ^{13}C NMR: δ 57.8 (OMe); 71.6 ($\equiv CH$); 72.6 (MeOCH$_2$); 87.1 ($\equiv C$-CH_2OMe); 128.4–134.9 (m, Ar, PPh_3); 201.7 (3CO); 204.9 (CO); 205.6 (CO). ^{31}P NMR: δ 54.0 (P–Co). IR: ν_{max} (film) 2922, 2061, 2004 and 1586 cm^{-1}. MS: m/z 590 (M^+), 562 (M^+–CO), 534 (M^+–2CO), 506 (M^+–3CO), 478 (M^+–4CO), 450 (M^+–5CO). Anal. Found (M^+): 589.9747. $C_{27}H_{21}Co_2O_6P$ Calc.: 589.9740.

3.7. Methylpropiolatepentacarbonyltriphenylphosphinedicobalt complexes 2d

Thermally: **1d** (96 mg, 0.26 mmol), PPh_3 (67 mg, 1 equiv.) in toluene (10 ml) gave **2d** (99 mg, 64%).

Photolytically: **1d** (125 mg, 0.34 mmol), PPh_3 (89 mg, 1 equiv.) in toluene (100 ml) gave **2d** (171 mg, 64%).

R_f 0.4, 30% ether–petrol. ^1H NMR: δ 3.38 (3H, s, CH_3); 5.23 (1H, d, $J = 4.7$, $\equiv CH$); 7.19–7.45 (15H, m, Ar, PPh_3). ^{13}C NMR: δ 52.0 (OMe); 71.4 ($\equiv CH$); 72.2 ($\equiv CCOOMe$); 128.4–134. (m, Ar, PPh_3); 170.5 (MeOCO); 200.2 (3CO); 204.4 (2CO). ^{31}P NMR: 54.9 (P–Co). IR: ν_{max} (film) 2923, 2072, 2015.5 1942.2, 1698.2, 1199.1, 1093.9 cm^{-1}. MS: m/z 604 (M^+), 548 (M^+–CO), 520 (M^+–2CO), 492 (M^+–3CO), 464 (M^+–4CO), 406 (M^+–5CO). Anal. Found (M^+): 603.9521. $C_{27}H_{19}Co_2O_7P$ Calc.: 603.9532.

3.8. 3-Butyne-2-onepentacarbonyltriphenylphosphinedicobalt complexes 2e

Thermally: **1e** (210 mg, 0.59 mmol), PPh_3 (160 mg, 1 equiv.) in toluene (10 ml) gave **2e** (170 mg, 60%).

Photolytically: **1e** (83 mg, 0.23 mmol), PPh_3 (61 mg, 1 equiv.) in toluene (100 ml) gave **2e** (116 mg, 96%).

R_f 0.36, 20% ether–petrol. ^1H NMR: δ 3.45 (3H, s, CH_3); 5.24 (1H, d, $J = 4.9$, $\equiv CH$); 7.27–7.44 (15H, m, Ar, PPh_3). ^{13}C NMR: δ 29.7 (CH_3); 71.7 ($\equiv CH$); 79.7 ($\equiv CCOCH_3$); 128.2–134.3 (m, Ar, PPh_3); 200.3 (3CO); 204.4 (2CO); acyl CO invisible or coincident. IR: ν_{max} (film) 2932, 2087.8, 2015.2, 1652.2 cm^{-1}. MS: m/z 589 (MH$^+$), 561 (M^+–CO), 533 (MH$^+$–2CO), 505 (MH$^+$–3CO), 477 (MH$^+$–4CO), 449 (MH$^+$–5CO). Anal. Found (M^+): 587.9565. $C_{27}H_{19}Co_2O_6P$ Calc.: 587.9583.

References and notes

[1] C. Viney, M. Phil Thesis, University of Sheffield, 1996.
[2] R.S. Dickson and P.J. Fraser, Adv. Organomet. Chem., 12 (1974) 323.
[3] L.S. Chai, W.R. Cullen, M. Franklin and A.R. Manning, Inorg. Chem., 14 (1975) 2521.
[4] A.M. Hay, W.J. Kerr, G.G. Kirk and D. Middlemiss, Organometallics, 14 (1995) 4986.
[5] For a review on the Pauson–Khand reaction see N.E. Schore, in B.M. Trost and I. Fleming (eds.), Comprehensive Organic Synthesis, Vol. 5, Pergamon, Oxford, 1991, p. 1307 and references cited therein.

[6] J.A. Dunn and P.L. Pauson, *J. Organomet. Chem.*, *355* (1991) 383.

[7] R.F. Heck, *J. Am. Chem. Soc.*, *85* (1963) 657.

[8] M. Arewgoda, B.H. Robinson and J. Simpson, *J. Am. Chem. Soc.*, *105* (1983) 1893.

[9] See J.P. Collman; L.S. Hegedus; J.R. Norton and R.G. Finke, in *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.

[10] This reaction is only discussed in the experimental section and no yield is given. D.A. Harbourne and F.G.A. Stone, *J. Chem. Soc. A*, (1968) 765.

[11] W.J. Kerr, G.G. Kirk and D. Middlemiss, *J. Organomet. Chem.*, *519* (1996) 93.

[12] See V. Varghese, M. Saha and M. Nicholas, *Org. Synth.*, *67* (1988) 141.

[13] M.F. D'Agostino, C.S. Frampton and M.J. McGlinchey, *Organometallics*, *9* (1990) 2972.